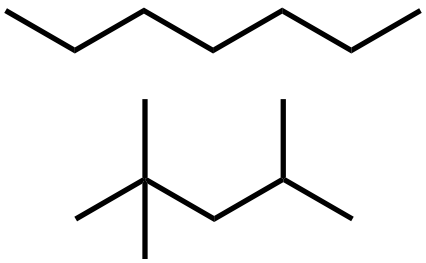
Development of Simplified Reaction Model Based on RO_2 and H_2O_2 Chemistry

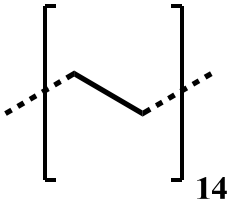
Yasuyuki Sakai, Hiromitsu Ando

University of Fukui, Japan

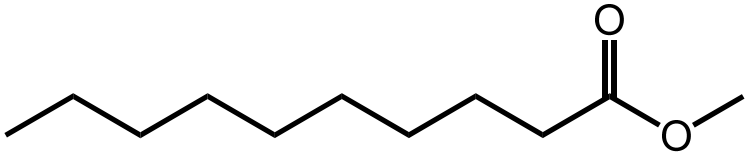
Detailed Chemical Kinetic Model



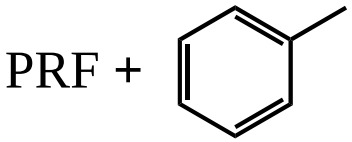
PRF; Primary Reference Fuel
(*n*-heptane and *iso*-octane)
1034 species 4236 reactions
H. J. Curran *et al.* (2002)



***n*-Hexadecane**
2116 species 8130 reactions
C. K. Westbrook *et al.* (2009)



Methyldecanoate
2878 species 8555 reactions
O. Herbinet *et al.* (2008)



Gasoline Surrogate (PRF + Toluene)
783 species 2883 reactions
Y. Sakai *et al.* (2009)

Problems: Numerical Simulation of Reactive Flow

High Computational Costs

- Large number of equations being solved
- Stiffness

Mechanism Reduction

- **DRG** (Directed Relation Graph) T. Lu *et al.* (2005)
- **PCA** (Principal Component Analysis) S. Vajda *et al.* (1985)
- **CSP** (Computational Singular Perturbation) S. H. Lam *et al.* (1994)
- **ILDM** (Intrinsic Low-Dimensional Manifold) U. Mass *et al.* (1992)
- **RCCE** (Rate-Controlled Constrained Equilibrium) J. C. Keck *et al.* (1990)
- **Lumping** R. Ogink *et al.* (2002) *etc.*

No estimation method for lumped reactions and rate constants
Not applicable over the wide range of T, p, φ *Fuel*.

Objective

Detailed Model

↓

Universal Rule for hydrocarbon ignition H. Ando *et al.* (2009)

↓

Universal Lumping Method (T, p, φ, Fuel)

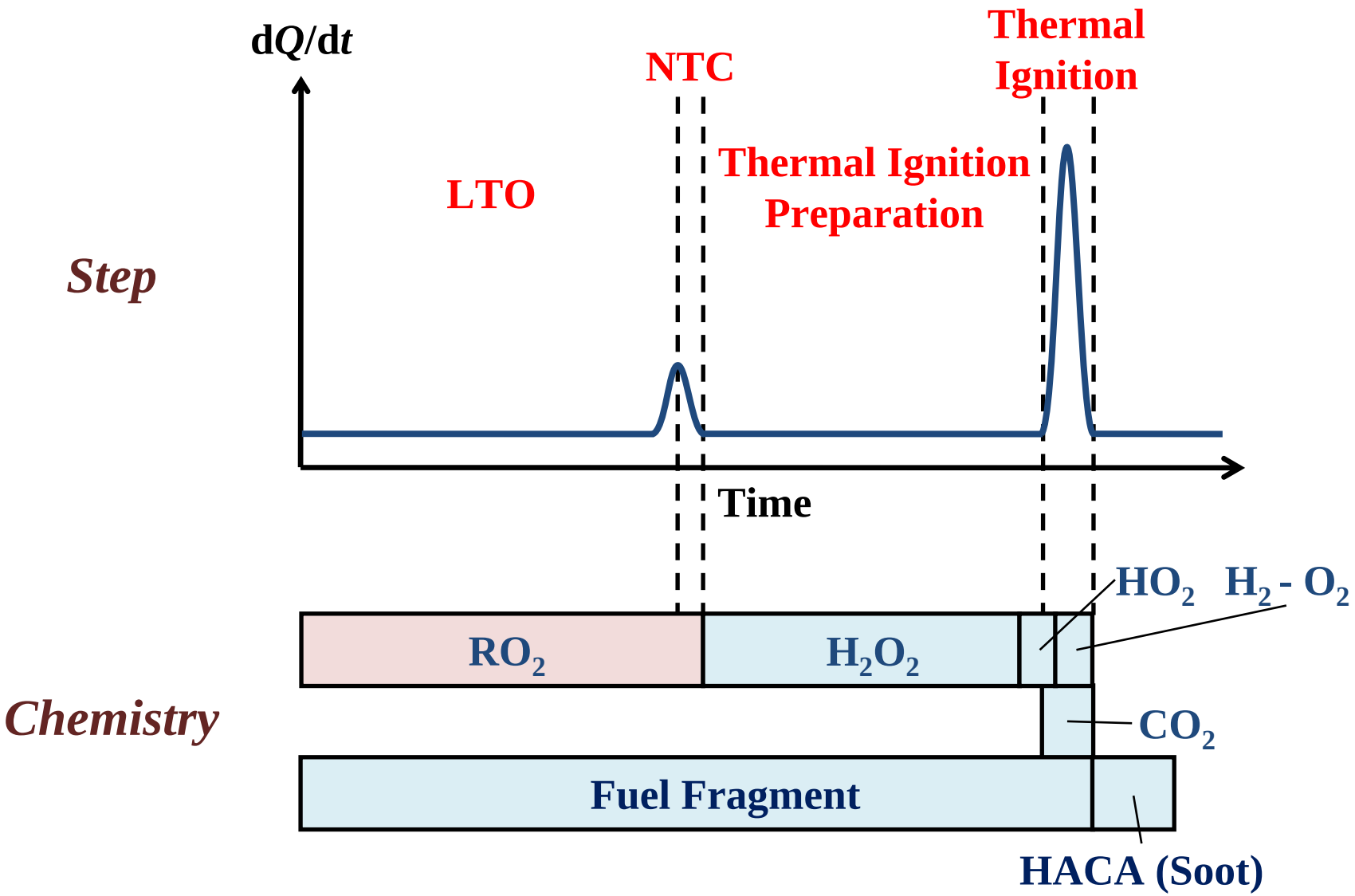
↓

(Alkane) Simplified Model

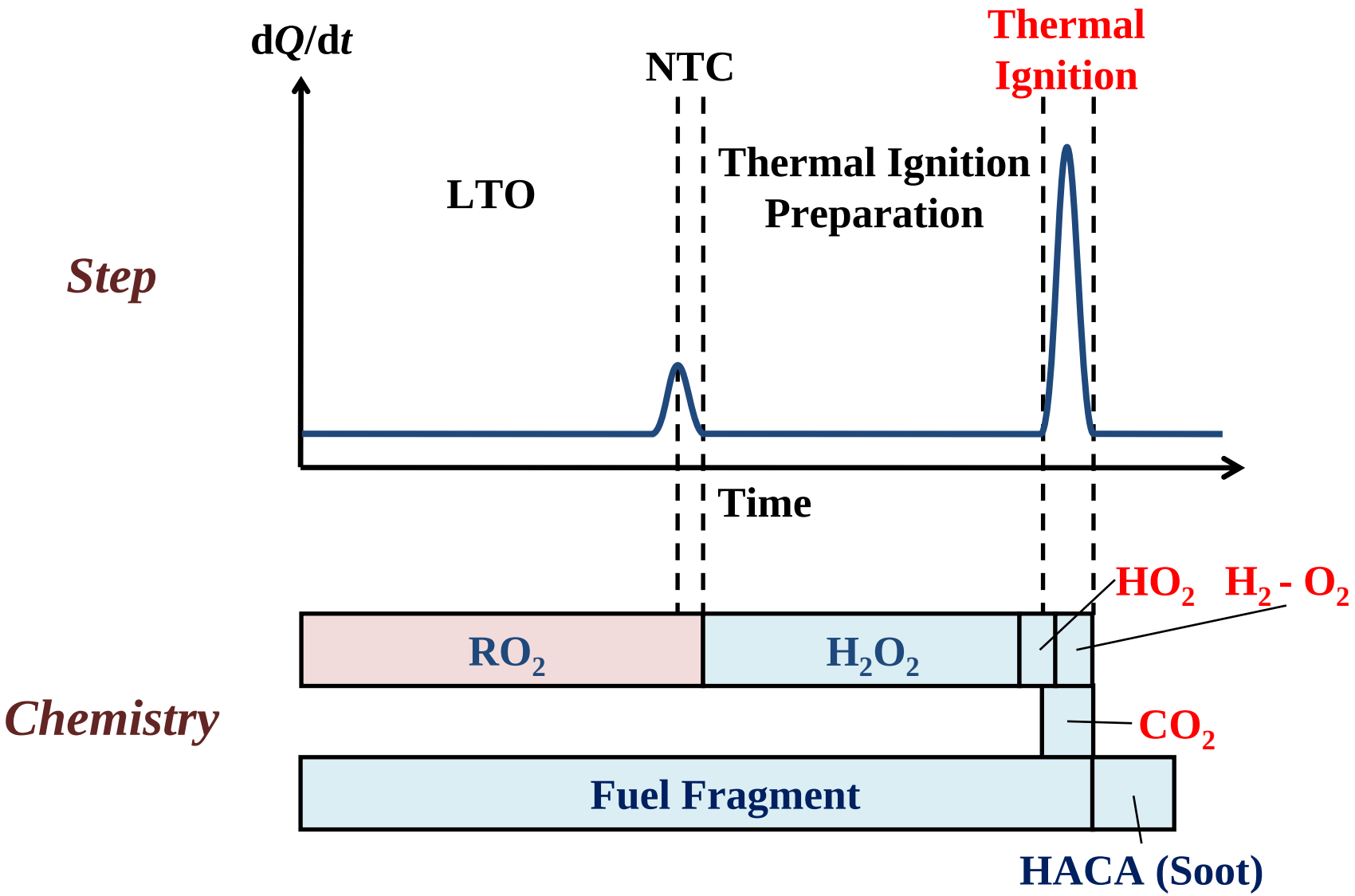
Method

- **Solver**
  - **CHEMKIN PRO**
- **Ignition delay times, τ**
  - **Ignition (T_p=1600 K) in adiabatic constant volume vessel**
- **Model validation**
  - **τ(Detailed Model)↔τ(Simplified Model)**

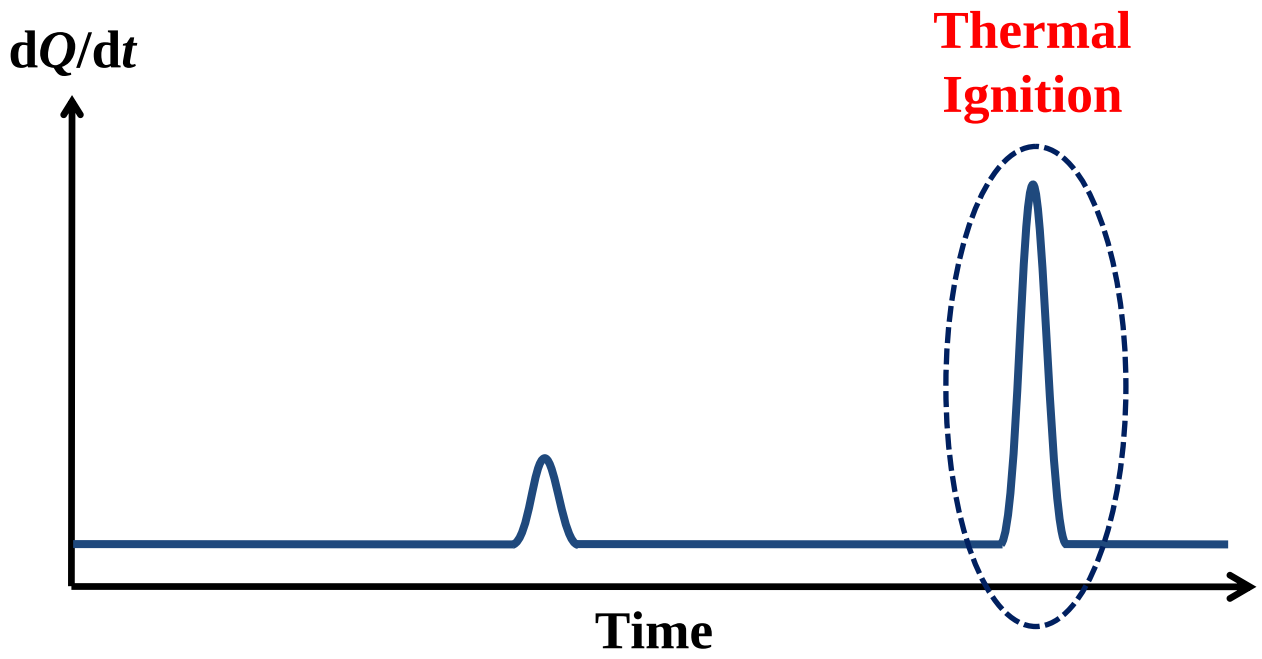
Reaction Regimes of Hydrocarbon Oxidation



Reaction Regimes of Hydrocarbon Oxidation



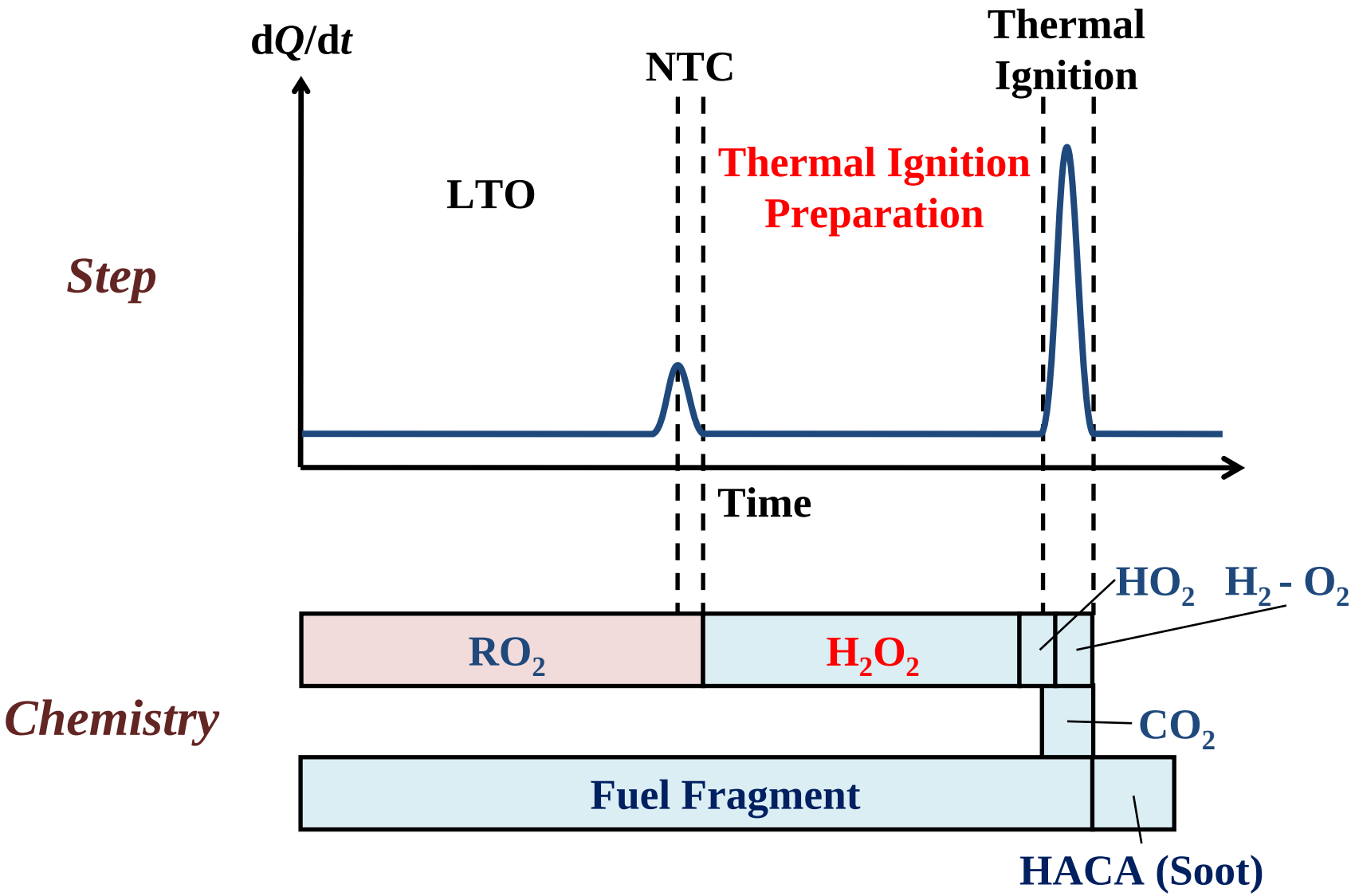
HO_2, H_2–O_2, CO_2 Chemistry



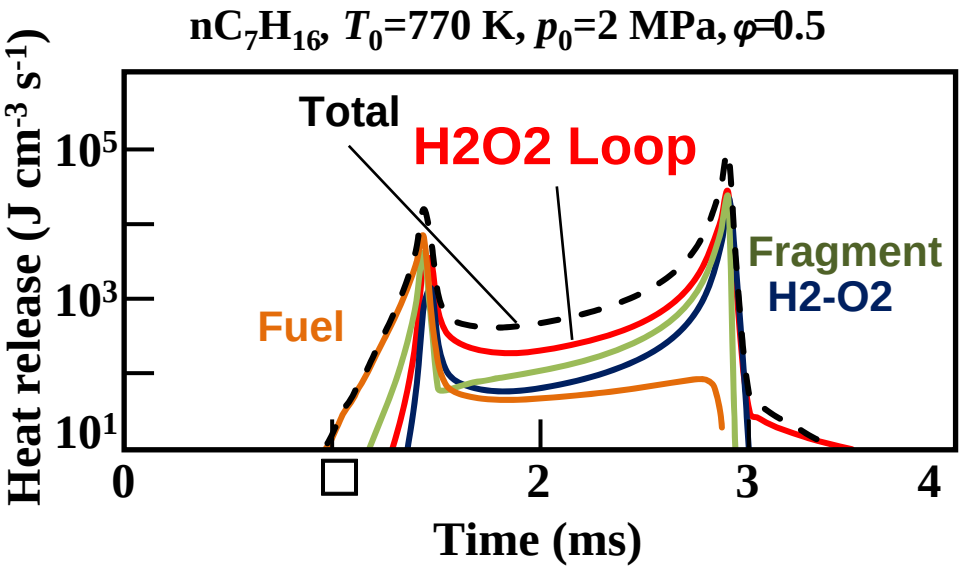
Dominant Reactions

$H+O_2=O+OH$	$H_2O_2(+m)=OH+OH(+m)$
$H+O_2(+M)=HO_2(+M)$	$HO_2+H=OH+OH$
$H_2+M=H+H+M$	$HO_2+H=H_2+O_2$
$O_2+M=O+O+M$	$HO_2+O=OH+O_2$
$OH+M=O+H+M$	$H_2O_2+H=H_2+HO_2$
$H_2O+M=H+OH+M$	$H_2O_2+O=OH+HO_2$
$O+H_2=H+OH$	$HO_2+OH=H_2O+O_2$
$O+H_2O=OH+OH$	$H_2O_2+OH=H_2O+HO_2$
$OH+H_2=H+H_2O$	$CO+OH=CO_2+H$

Reaction Regimes of Hydrocarbon Oxidation



H_2O_2 Chemistry



H_2O_2 Loop reactions

main loop

$H_2O_2(+m)=2OH(+m)$

$2CH_2O+2OH=2HCO+2H_2O$

$2HCO+2O_2=2CO+2HO_2$

$2HO_2=H_2O_2+O_2$

sub loop

$H+O_2(+M)=HO_2(+M)$

$HO_2+OH=H_2O+O_2$

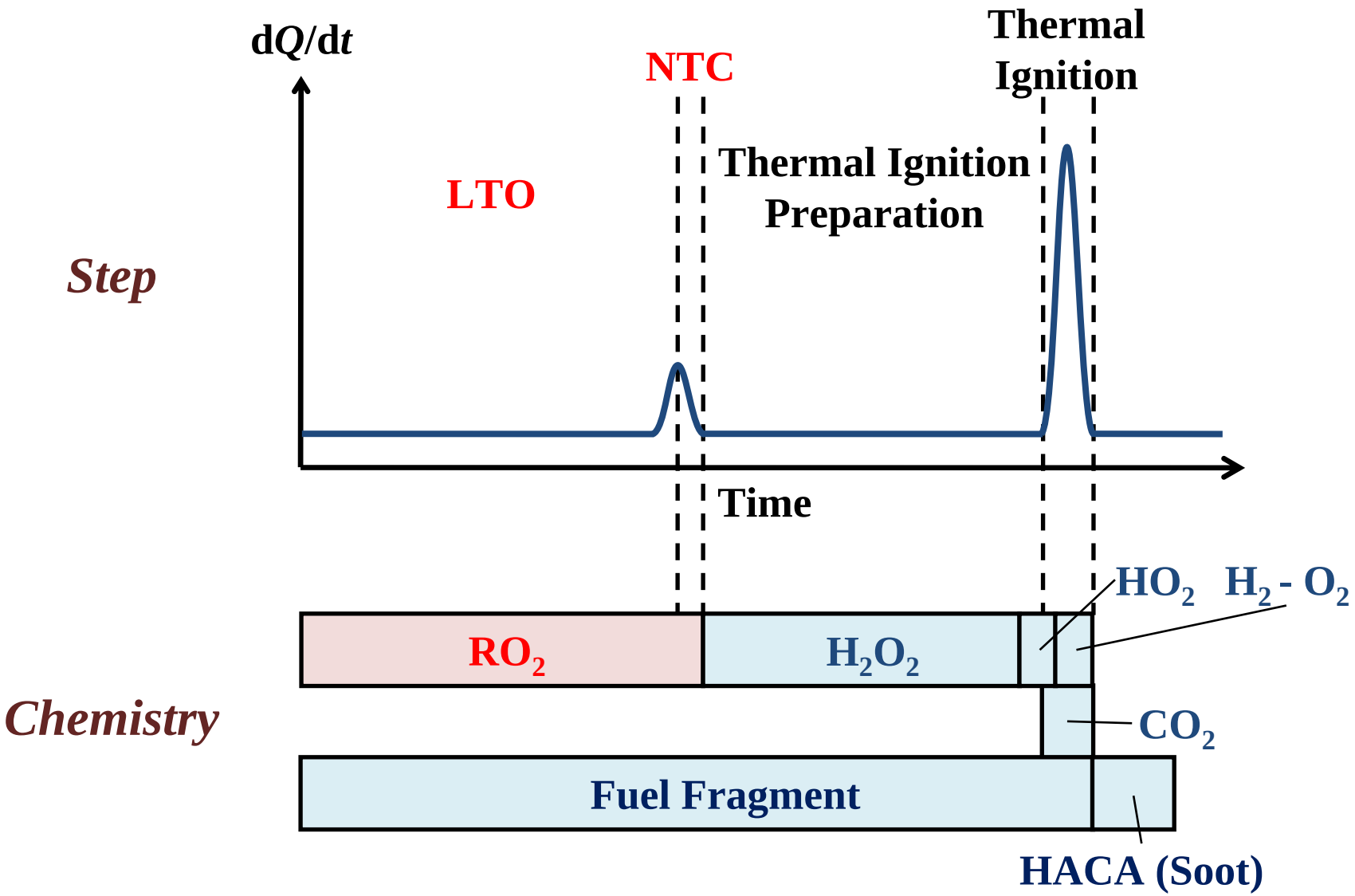
$H_2O_2+OH=H_2O+HO_2$

net reaction: $2CH_2O + O_2 = 2CO + 2H_2O +$ 436 kJ mol^{-1}

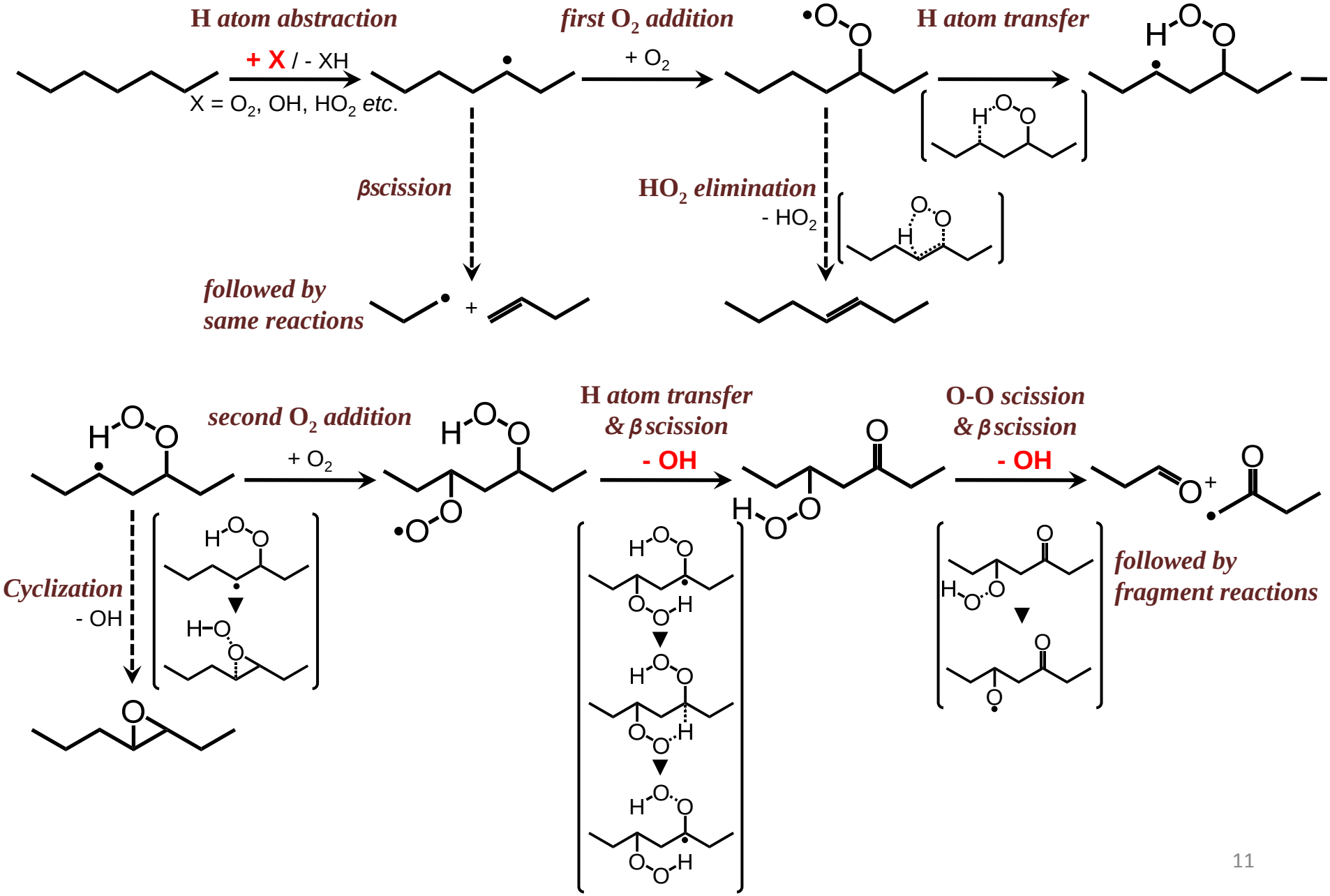
This heat release raise temperature to the thermal ignition.

Rate of heat release depends on $[H_2O_2]$.

Reaction Regimes of Hydrocarbon Oxidation



RO_2 Chemistry



RO_2 Chemistry

Transition from RO_2 chemistry to H_2O_2 chemistry

Chain Branching

$$nC_7H_{16}+OH \rightarrow Fragment+nOH$$

Chain Propagation

$$2CH_2O+2OH=2HCO+2H_2O$$

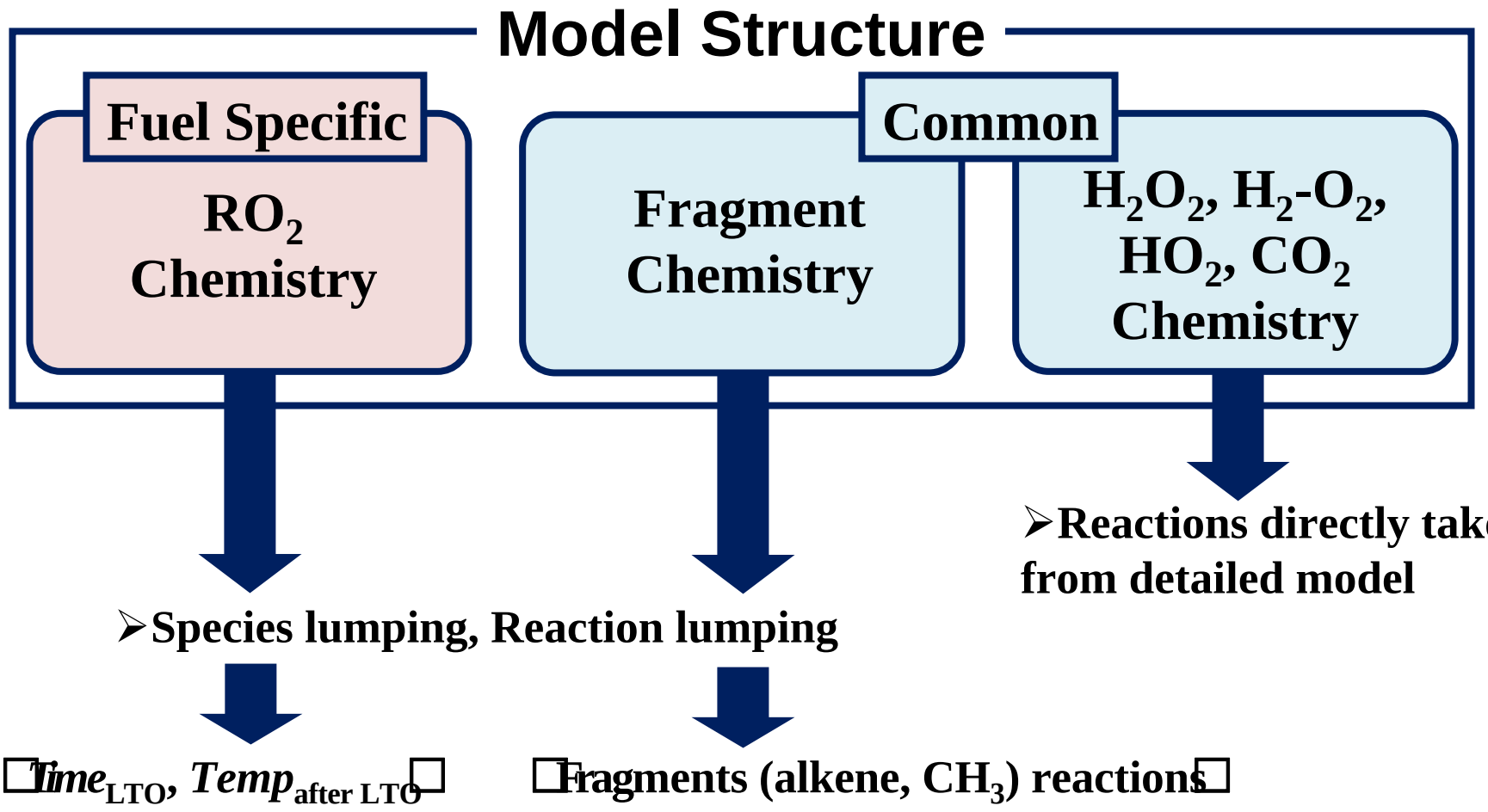
$$2HCO+2O_2=2CO+2HO_2$$

$$HO_2+HO_2=H_2O_2+O_2$$

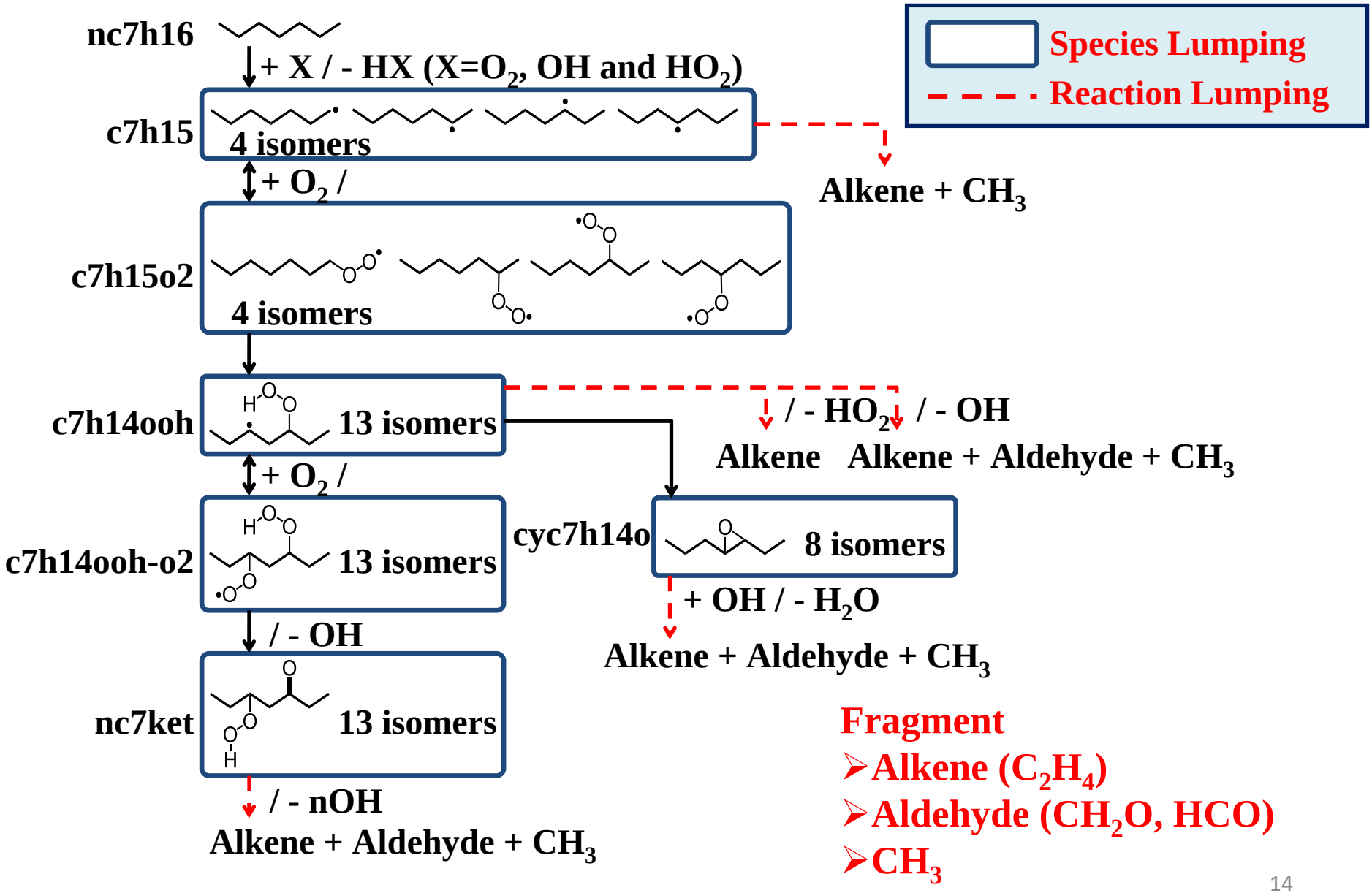
$$H_2O_2(+m)=2OH(+m)$$

$T_{\text{after LTO}}$ and $[H_2O_2]_{\text{after LTO}}$ determine the period of thermal ignition preparation and thermal ignition.

Universal Simplified Method



RO_2 Chemistry



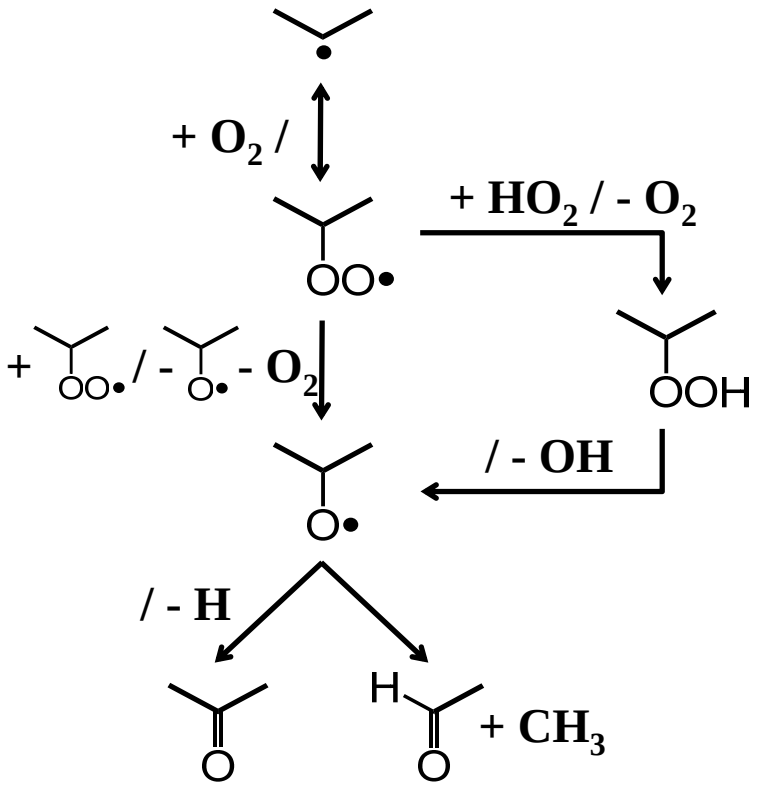
Fragment

- **Alkene (C_2H_4)**
- **Aldehyde (CH_2O, HCO)**
- **CH_3**

RO_2 Chemistry

RO_2 Radical Reactions (if there is no QOOH path via 6-ring TS)

ex.) $C_3H_8 \rightarrow iC_3H_7$



Alkane oxidations, that this RO_2 radical is main intermediate, are rare case.

RO_2 Chemistry

Rate Constants of RO_2 Chemistry Reactions

$RH+O_2 \rightarrow R+HO_2$	Sum of isomers
$RH+OH \rightarrow R+H_2O$	Sum of isomers
$RH+HO_2 \rightarrow R+H_2O_2$	Sum of isomers
$R+O_2 \rightarrow RO_2$	Average of isomers
$RO_2 \rightarrow QOOH$	Average of isomers
$QOOH \rightarrow Alkene+HO_2$	Min of isomers
$QOOH \rightarrow cyEther+OH$	Min of isomers
$QOOH \rightarrow Alkene+Aldehyde+CH_3+OH$	Average of isomers
$QOOH+O_2 \rightarrow O_2QOOH$	Average of isomers
$O_2QOOH \rightarrow Ket+OH$	Max of isomers
$Ket \rightarrow alkene+aldehyde+CH_3+nOH$	Average of isomers
$cyEther+OH \rightarrow Alkene+Aldehyde+CH_3+H_2O$	Average of isomers
$R \rightarrow Alkene+CH_3$	Average of isomers

For each fuel, Rate constants and product ratios are parameter to coincide with the time and temperature of LTO predicted by detailed model. (strictly not universal method)

Fragment Chemistry (Alkene)

Alkene → C_2H_4 + C_3H_6

$$C_nH_{2n} \rightarrow \frac{n}{2}C_2H_4 \quad (n = \text{even})$$

$$C_nH_{2n} \rightarrow \frac{n-3}{2}C_2H_4 + C_3H_6 \quad (n = \text{odd})$$

ex.) $C_8H_{16} \rightarrow 4C_2H_4$

$C_7H_{14} \rightarrow 2C_2H_4 + C_3H_6$

$C_6H_{12} \rightarrow 3C_2H_4$

$C_5H_{10} \rightarrow C_2H_4 + C_3H_6$

$C_4H_8 \rightarrow 2C_2H_4$

Alkene → C_2H_4

$$C_nH_{2n} \rightarrow \frac{n}{2}C_2H_4$$

ex.) $C_8H_{16} \rightarrow 4C_2H_4$

$C_7H_{14} \rightarrow 3.5C_2H_4$

$C_6H_{12} \rightarrow 3C_2H_4$

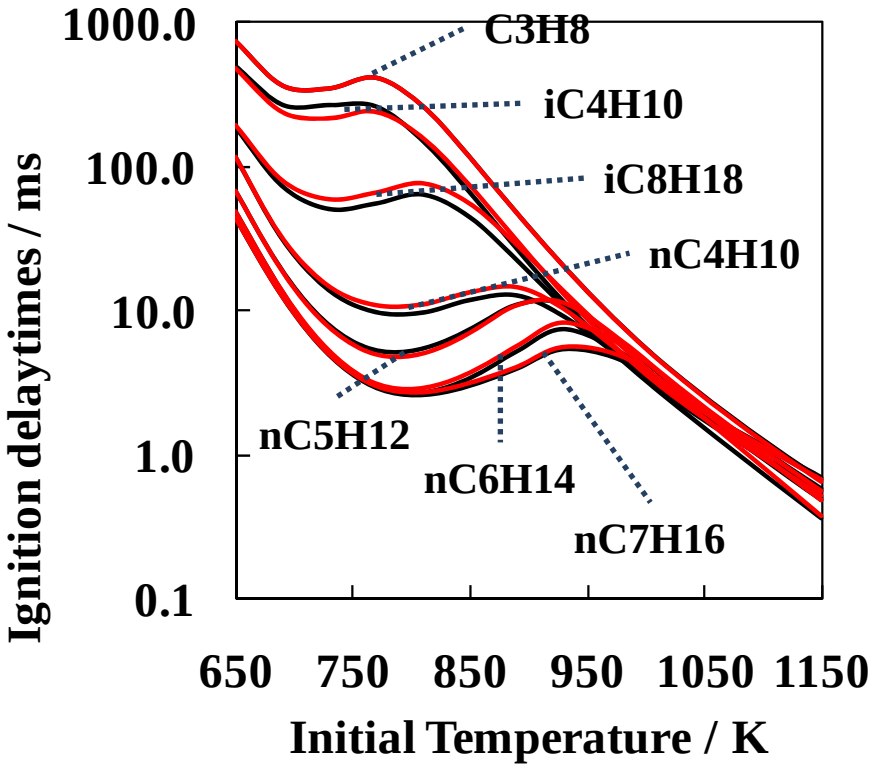
$C_5H_{10} \rightarrow 2.5C_2H_4$

$C_4H_8 \rightarrow 2C_2H_4$

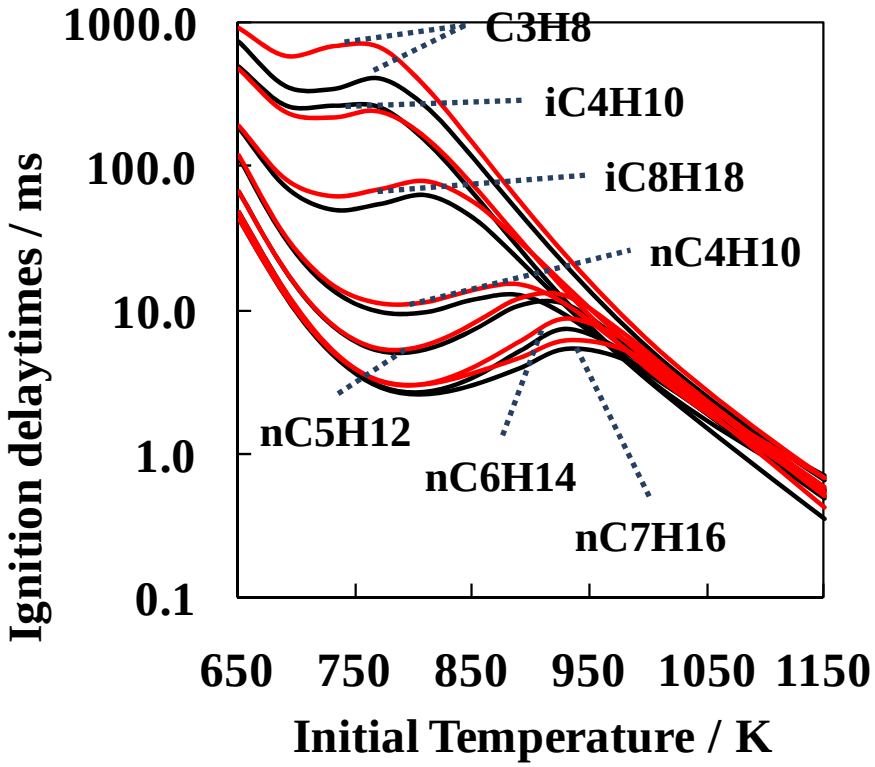
$C_3H_6 \rightarrow 1.5C_2H_4$

Fragment Chemistry (Alkene)

Alkene → C_2H_4

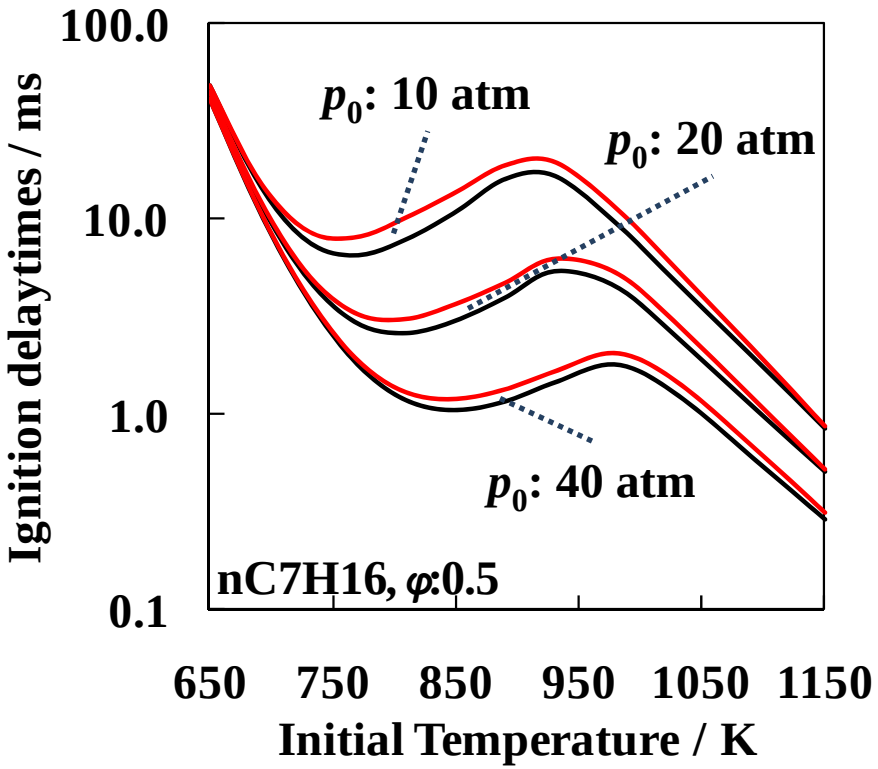


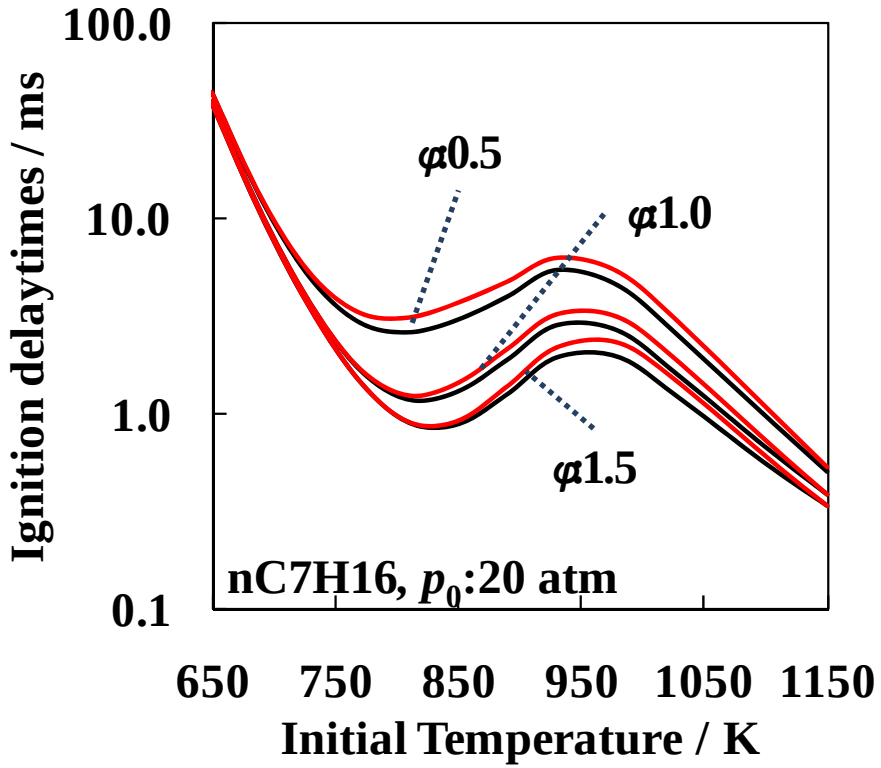
Alkene → C_2H_4 + C_3H_6



Fragment Chemistry (Alkene)

Alkene→C_2H_4





Fragment Chemistry (Alkene)

C_2H_4 →lumping reactions

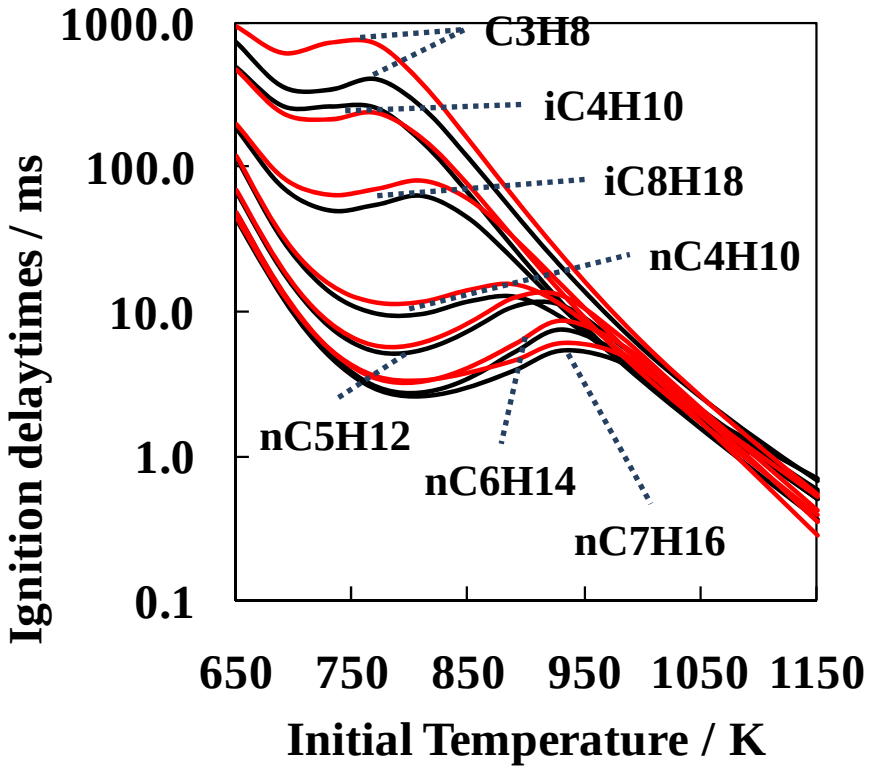
C_2H_4 oxidation path between 950 and 2000 K at initial conditions T_0: 770 K, p_0: 20 atm, φ:0.5, Fuel: nC_7H_{16}

c2h4	41	oh/h2o	c2h3	37	o2/o	ch2cho	87	o2/co,oh	ch2o										
							59	o/h	hcco	92	o2/co2	hco							
				31	o2/ho2	c2h2				41	/	ch2(s)	99	o2/co,oh,h					
							25	o/co	ch2(s)	29	o2/co,h2o								
										18	co/	ch2co	47	oh/co	ch2oh	98	o2/ho2	ch2o	
													36	oh/h2o	hcco	92	o2/co2	hco	
													10	h/h2	hcco	92	o2/co2	hco	
							13	o2/oh	hcco	92	o2/co2	hco							
				30	o2/	ch2o													
						hco													
	27	o/	ch3																
			hco																

ch2o	65	oh/h2o	hco	80	o2/co,ho2			
				18	/h,co			
	11	oh/	hoch2o	100	/h	hocho	57	oh/h2o,co2,h
							16	oh/h2o,co,oh

Fragment Chemistry (Alkene)

C_2H_4 →lumping reactions

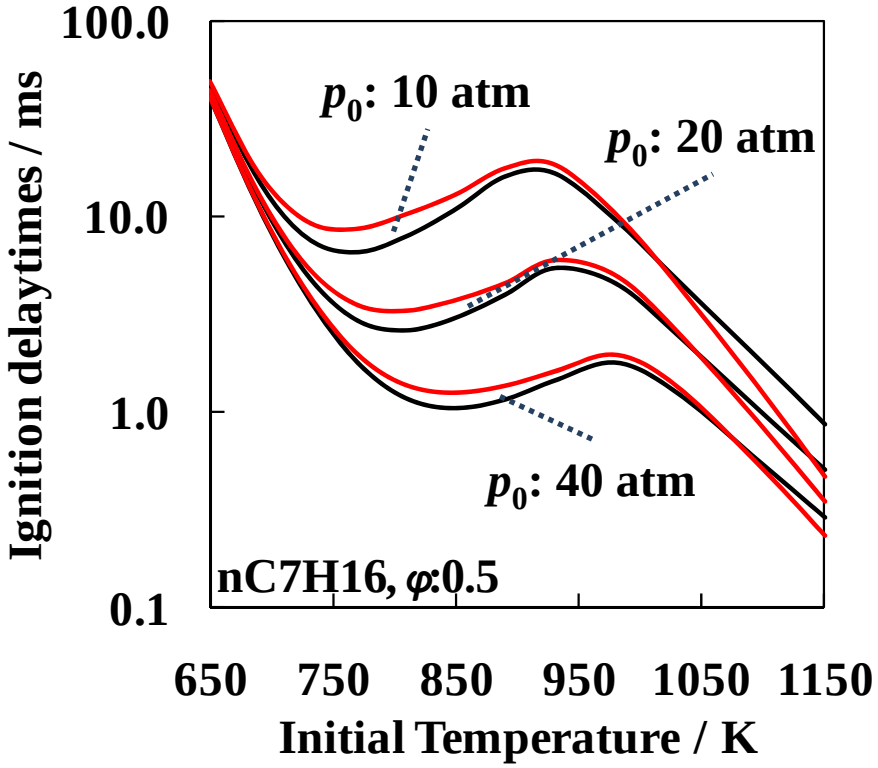


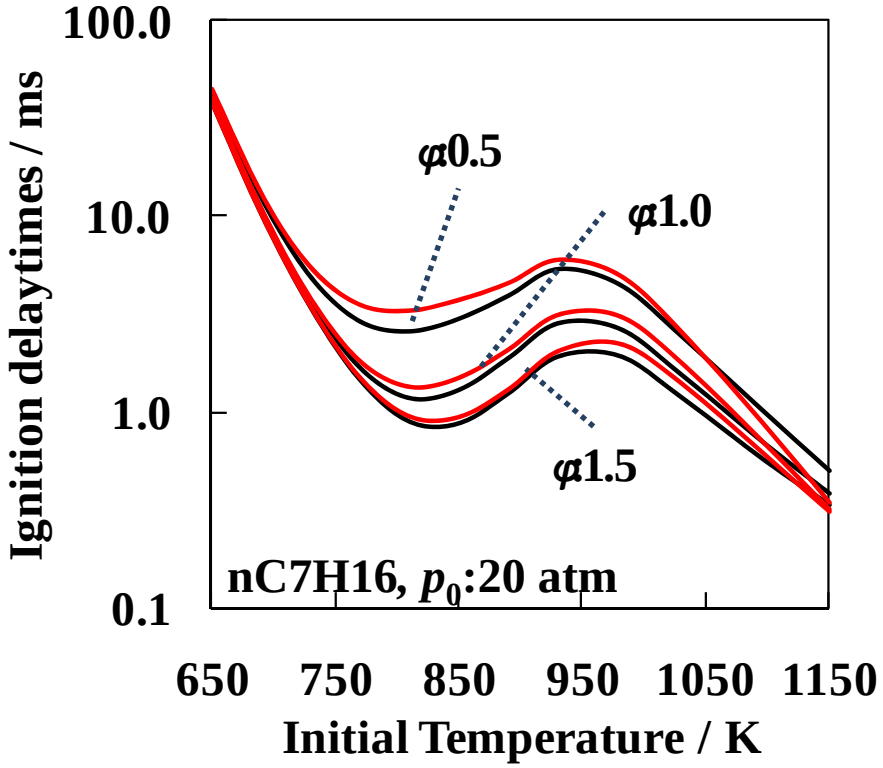
$$C_2H_4 + OH \rightarrow CH_3 + HCO + H \quad k = 2.02 \times 10^{13} \exp\left(-\frac{5955}{RT}\right)$$

$$C_2H_4 + O_2 \rightarrow 2CO + 4H \quad k = 4.0 \times 10^{16} \exp\left(-\frac{54000}{RT}\right)$$

Fragment Chemistry (Alkene)

C_2H_4 →lumping reactions





$$C_2H_4 + OH \rightarrow CH_3 + HCO + H \quad k = 2.02\times10^{13}\exp\left(-\frac{5955}{RT}\right)$$

$$C_2H_4 + O_2 \rightarrow 2CO + 4H \quad k = 4.0\times10^{16}\exp\left(-\frac{54000}{RT}\right)$$

Fragment Chemistry (CH_3)

$CH_3 \rightarrow$ lumping reactions

C_2H_4 oxidation path between 950 and 2000 K at initial conditions T_0: 770 K, p_0: 20 atm, φ:0.5, Fuel: nC_7H_{16}

ch3	<>	o2/	ch3o2	24	ch3/ch3o	ch3o	96	/h	ch2o			
				17	c3h5-a/c3h5o							
				8	c4h7/c4h7o							
				5	c2h5/c2h5o							
				12	ch2o/hco	ch3o2h	100	/oh	ch3o	96	/h	ch2o
				8	ch3cho/ch3co							
				6	ho2/o2							
				5	c2h5cho/c2h5co							
ch3	29	ho2/oh	ch3o	96	/h	ch2o						
	10	ho2/o2	*ch4*									
	9	ch3/	*c2h6*									
	7	o/h	ch2o									
	7	oh/	*ch3oh*									
	6	o2/oh	ch2o									

Reaction path shown by red colors taken from detailed model.

n-Heptane Model

25 Species

h h2 o o2 oh h2o ho2 h2o2 n2 co co2 hco ch2o ch3 ch3o ch3o2 ch3o2h c2h4
nc7h16 c7h15 c7h15o2 c7h14ooh c7h14ooh-o2 nc7ket cyc7h14o

50 Reactions

< H_2-O_2, HO_2, CO_2 >

(R1) h2+m=h+h+m
(R2) o2+m=o+o+m
(R3) oh+m=o+h+m
(R4) h2o+m=h+oh+m
(R5) h+o2=o+oh
(R6) o+h2=h+oh
(R7) o+h2o=oh+oh
(R8) oh+h2=h+h2o
(R9) ho2+h=oh+oh
(R10) ho2+h=h2+o2
(R11) ho2+o=oh+o2
(R12) h2o2+h=h2o+oh
(R13) h2o2+h=h2+ho2
(R14) h2o2+o=oh+ho2
(R15) co+oh=co2+h

< H_2O_2 >

(R16) h+o2(+m)=ho2(+m)
(R17) ho2+oh=h2o+o2
(R18) h2o2+oh=h2o+ho2, duplicate
(R19) h2o2+oh=h2o+ho2, duplicate
(R20) oh+oh(+m)=h2o2+(m)
(R21) ch2o+oh=hco+h2o
(R22) hco+o2=co+ho2
(R23) h2o2+o2=ho2+ho2, duplicate
(R24) h2o2+o2=ho2+ho2, duplicate

< CH_3 (Fragment) >

(R25) ch3o2+m=ch3+o2+m
(R26) ch3+o=ch2o+h
(R27) ch3+ho2=ch3o+oh
(R28) ch3+o2=ch2o+oh
(R29) ch3o(+m)=ch2o+h(+m)
(R30) ch3o2+ch3=ch3o+ch3o
(R31) ch3o2+ch2o=ch3o2h+hco
(R32) ch3o2h=ch3o+oh

< RO_2 >

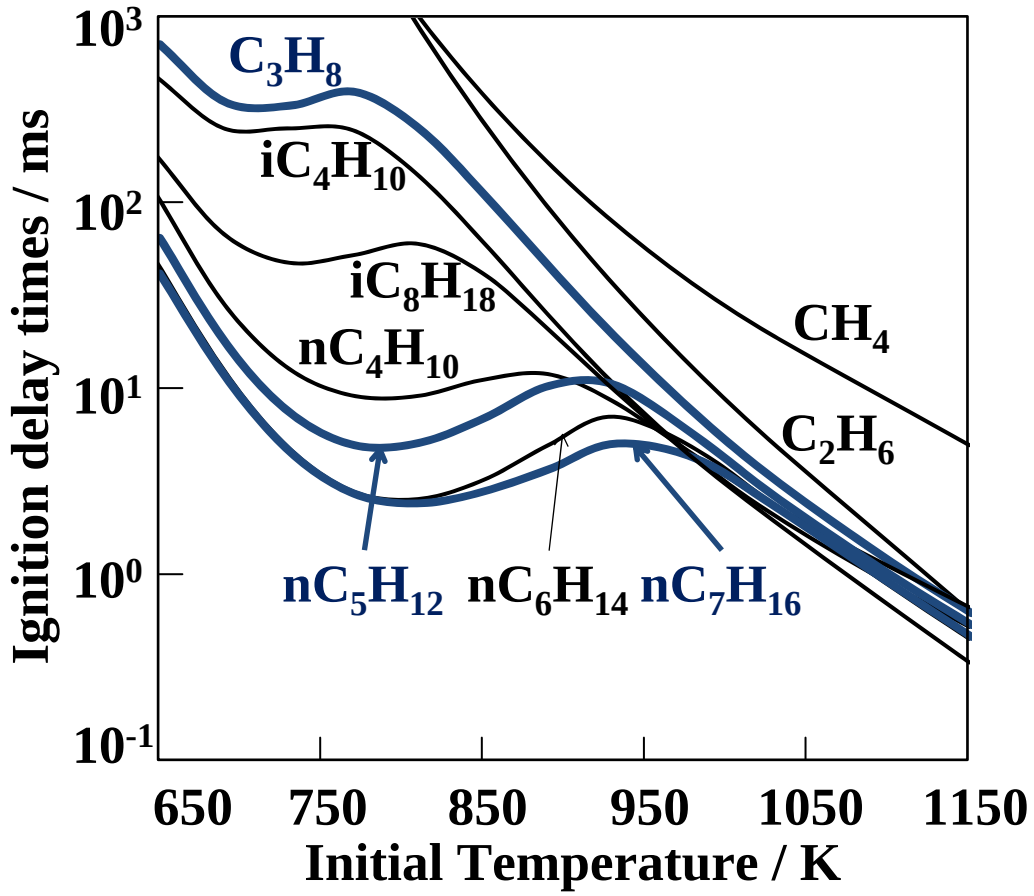
(R33) nc7h16+o2=>c7h15+ho2
(R34) nc7h16+oh=>c7h15+h2o
(R35) nc7h16+ho2=>c7h15+h2o2
(R36) c7h15+o2=c7h15o2
(R37) c7h15o2=>c7h14ooh
(R38) c7h14ooh=>2c2h4+c3h6+ho2
(R39) c7h14ooh=>cyc7h14o+oh
(R40) c7h14ooh=>ch2o+3c2h4+oh
(R41) c7h14ooh+o2=c7h14ooh-o2
(R42) c7h14ooh-o2=>nc7ket+oh
(R43) nc7ket=>2c2h4+ch3+oh+2hco
(R44) nc7ket=>2c2h4+3ch2o
(R45) nc7ket=>3c2h4+co+2oh
(R46) cyc7h14o+oh=>3c2h4+hco+h2o

< High temp. (Fragment) >

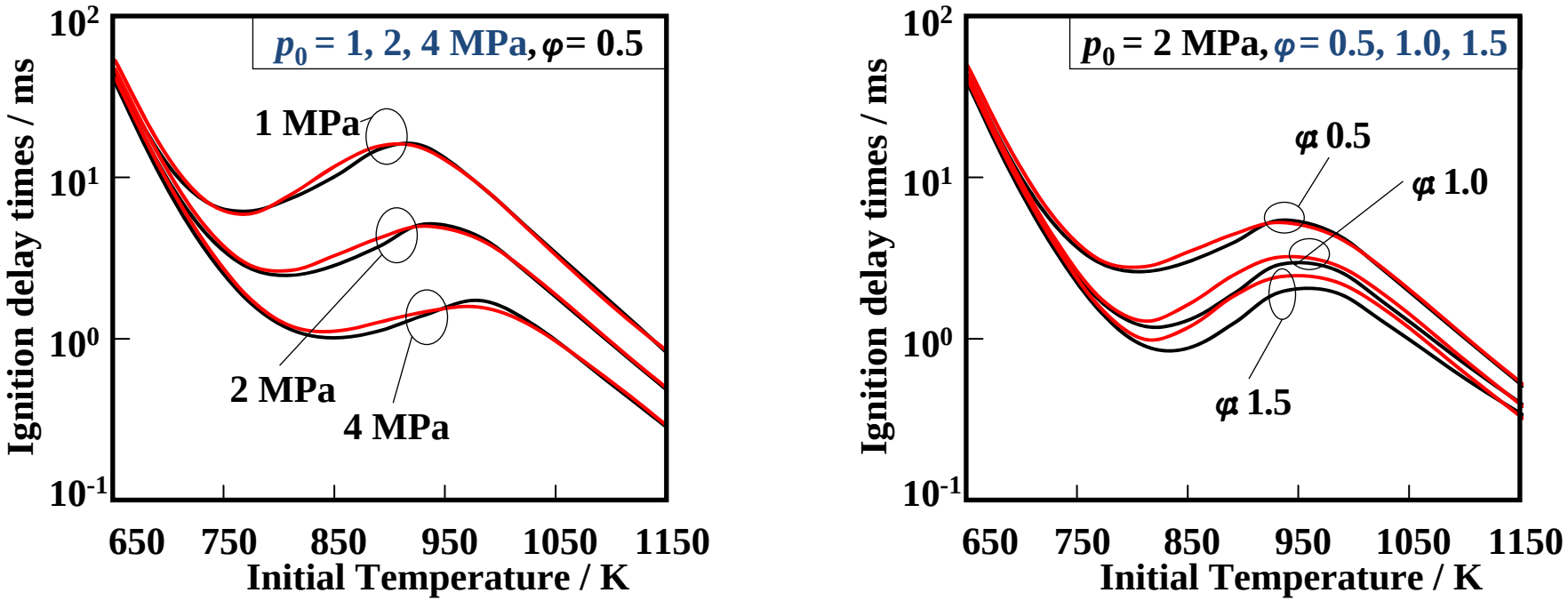
(R47) c2h4+oh=>hco+ch3+h
(R48) c2h4+o2=4h+2co
(R49) c7h15=>ch3+3c2h4
(R50) hco+m=>h+co+m

Validation

Selected linear alkanes (nC_7H_{16}, nC_5H_{12}, C_3H_8)



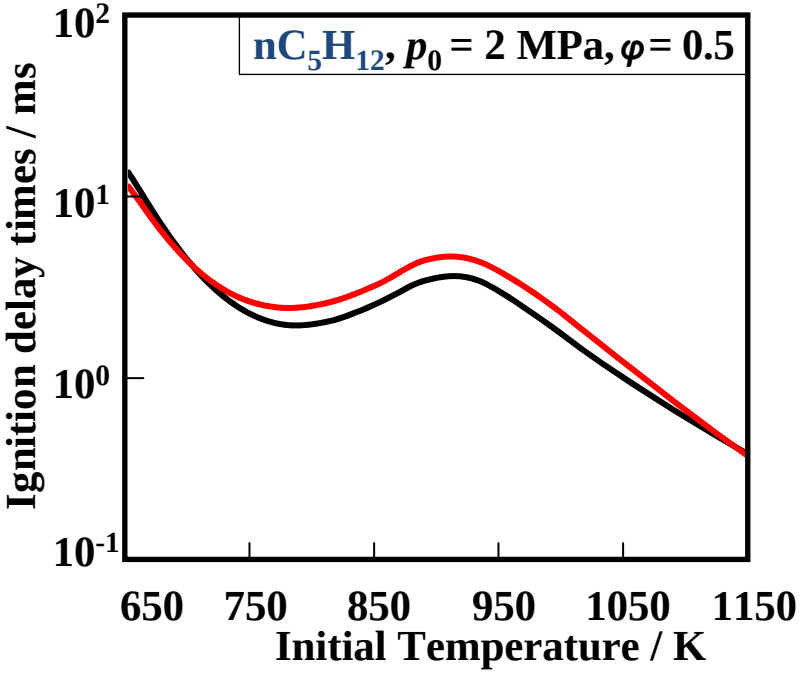
Ignition Delay Times (nC_7H_{16})

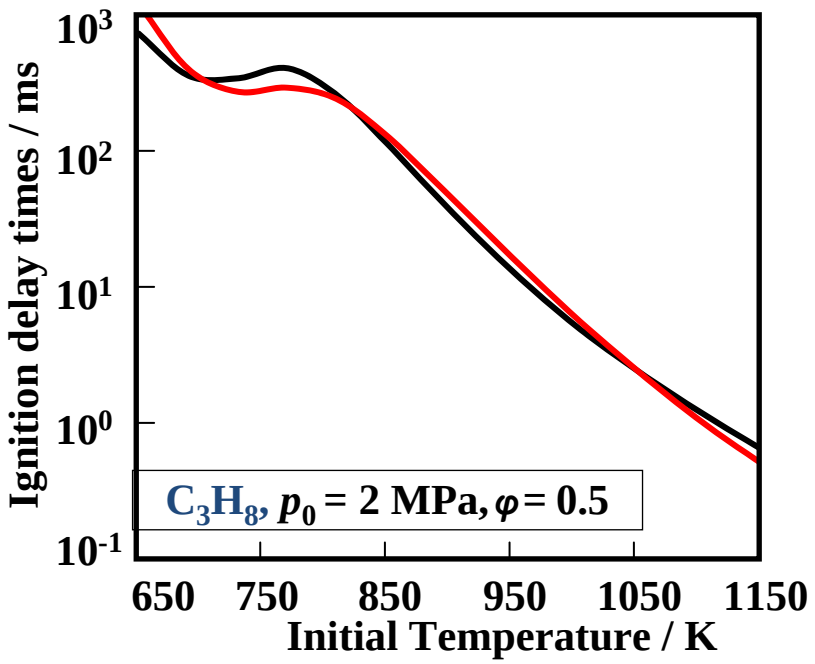


Simplified Model (25species, 50 reactions)

Full_LLNL Model (1034 species, 4236 reactions)

Ignition Delay Times

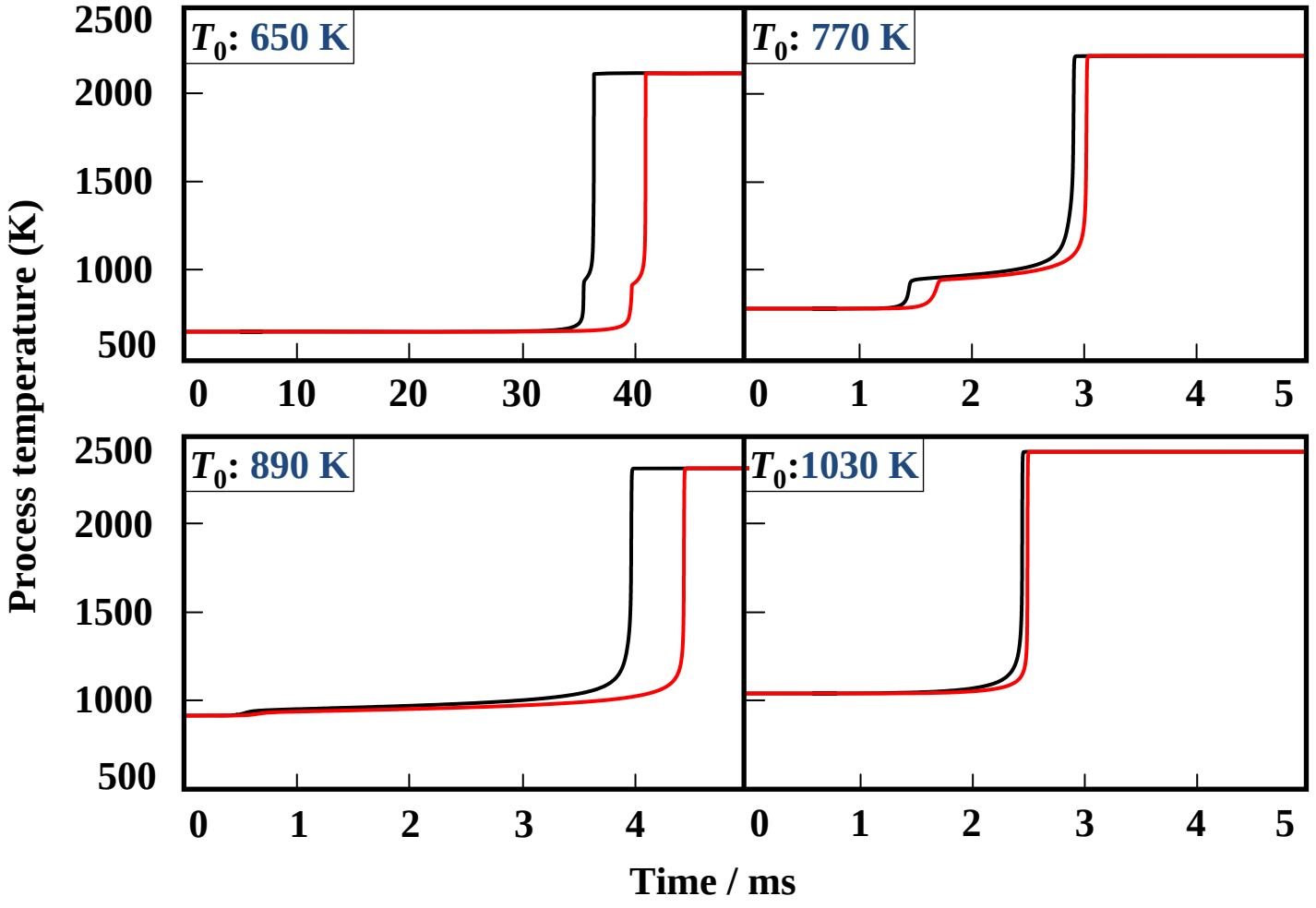




Simplified Model (25species, 50 reactions)(27 species, 55 reactions for C3H8)

Full_LLNL Model (1034 species, 4236 reactions)

Temperature Profile (nC_7H_{16}, p_0 = 2 MPa and φ= 0.5)



Summary

We have proposed the lumping method applicable over the wide range of conditions (*T*, *p*, φ, *Fuel*) based on the knowledge of RO_2, H_2O_2 chemistry. The simplified models constructed by this method contain only 25 species and 50 reactions.

Future Work

- **Universal Lumping Method for RO_2 Chemistry**
- **Alcohol, Ester□□□**
- **Mixtures**