KAUST Research Conference

Hydrogen-Based Mobility and Power

Explosion Limits and Energy Conversion in Flames of Hydrogen/Ammonia Mixtures

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Background

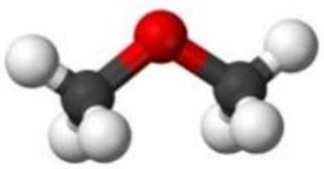
The Paris Agreement

Stricter limits on carbon emissions

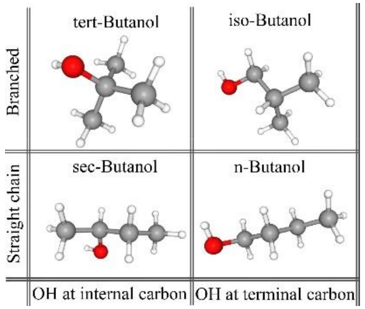
Alternative fuels

Low-carbon fuels

DME

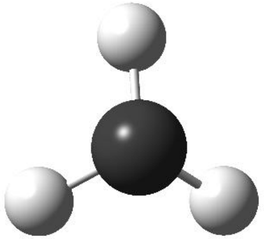


Butanol



Carbon-free fuels

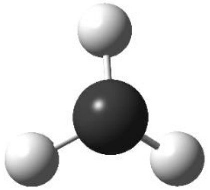
Ammonia

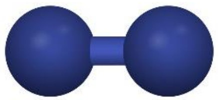


Hydrogen

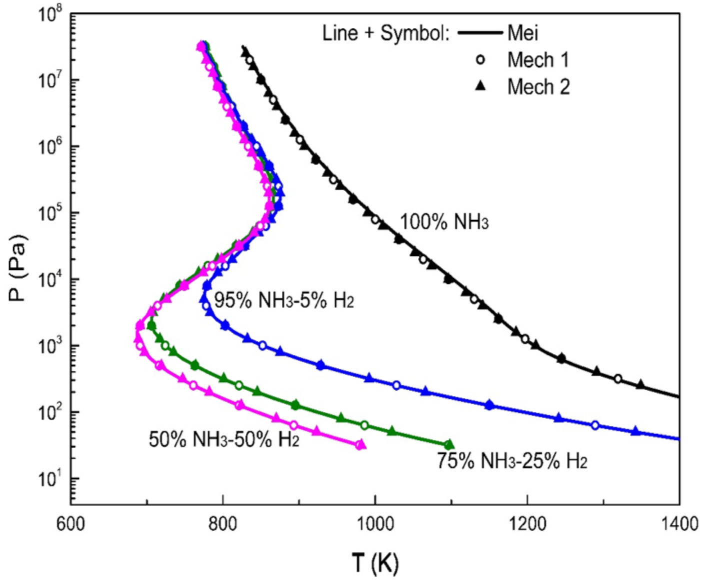
Background

Ammonia

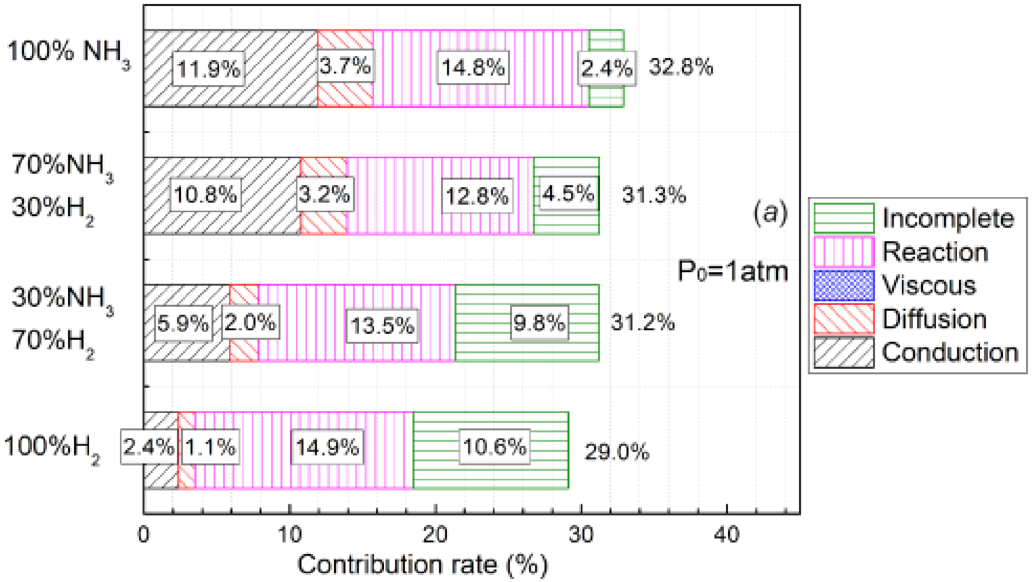




Hydrogen



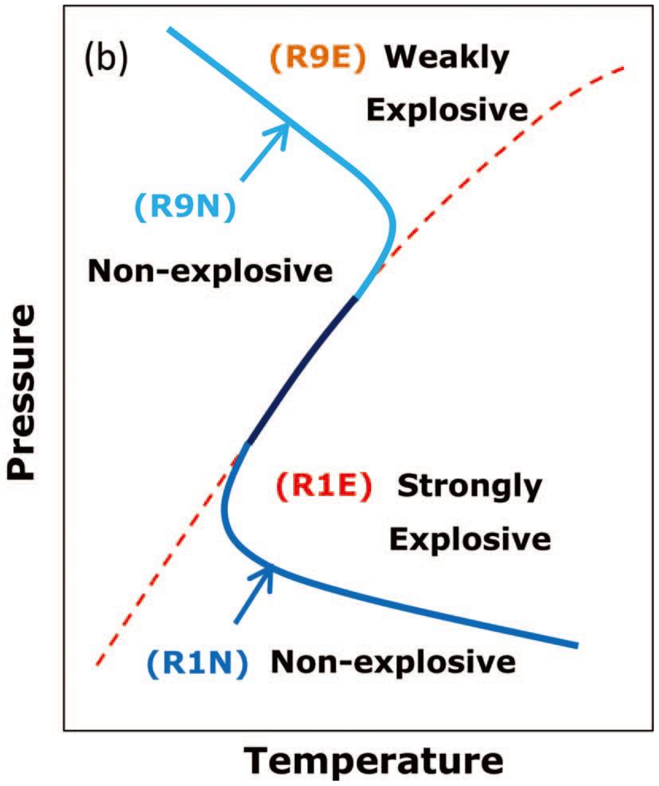
Explosion limits of changed binary mixtures



Exergy destruction sources in premixed flames

Part I: Explosion Limits of Hydrogen/ Ammonia Mixtures

Explosion Limits



The Structure of Explosion limits

Definition

- A pressure-temperature boundary separating the explosive and the nonexplosive regimes

Significance

- Important characteristics of homogenous fuel-oxidant systems
- To explore the critical conditions of chemical runaway
- To identify the controlling reactions in explosion
- To form the foundational block of fuel oxidation

Wang, X. et al. J CHEM PHYS, 2013.

Contents

Explosion Limits

↓

Sensitivity Analysis | Eigenvalue Analysis | Linear Theory

↓

Linear + Nonlinear Reduced Mechanism

Calculation Specification

01 **Calculation Model**

An adiabatic homogeneous zero-dimensional spherical reactor with radius of 3.7 cm; stoichiometric NH_3-H_2-O_2 mixtures

02 **Chemical Kinetics**

Mei mechanism (2019) with 38 species and 265 reactions

03 **Explosion Criterion**

50 K increments during 0.5s in the reactor

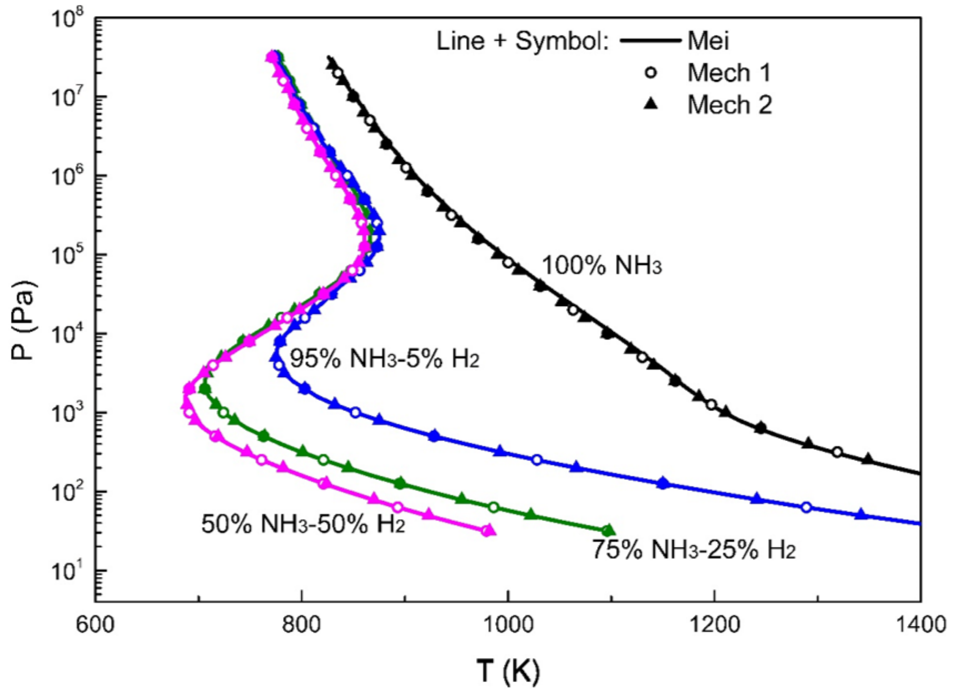
04 **Mechanism reduction methods**

Directed relation graph (DRG) and sensitivity analysis (SA)

Simulation: detailed& reduced mechanisms

Mei's mechanism —DRG→ **Mech 1** —SA→ **Mech 2**

(38 species, 265 reactions) (26 species, 188 reactions) (26 species, 82 reactions)



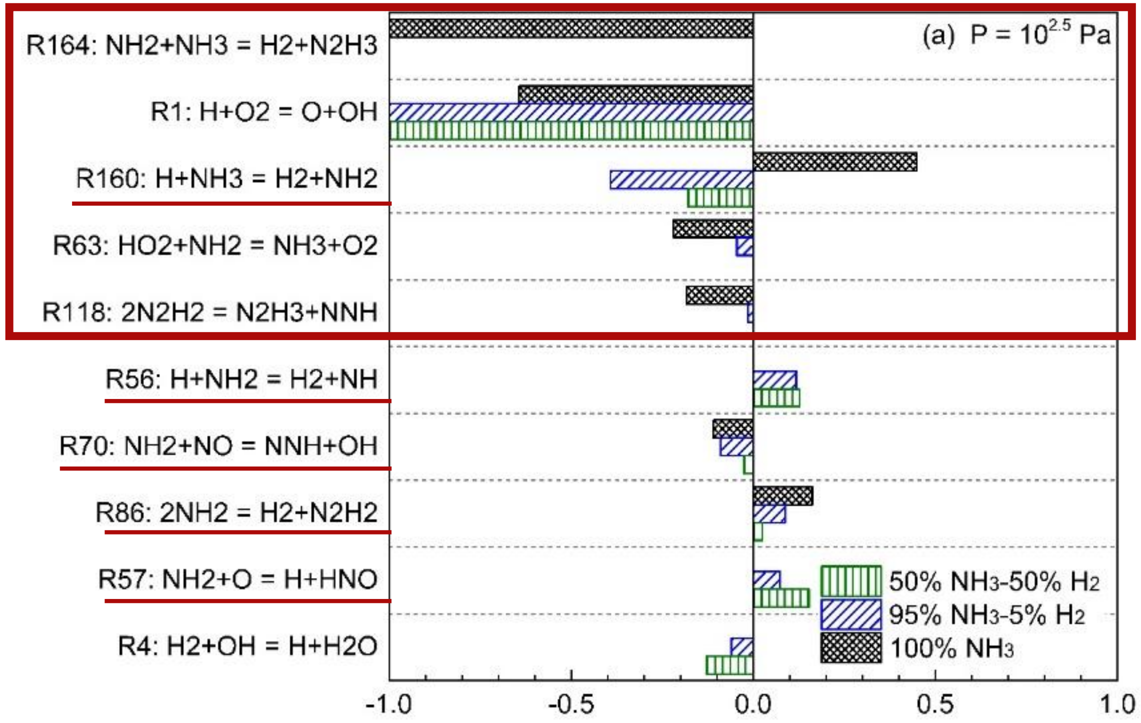
- **With H_2 addition**

Monotonic curve → Z-shaped curve

- **Higher H_2 percentage**

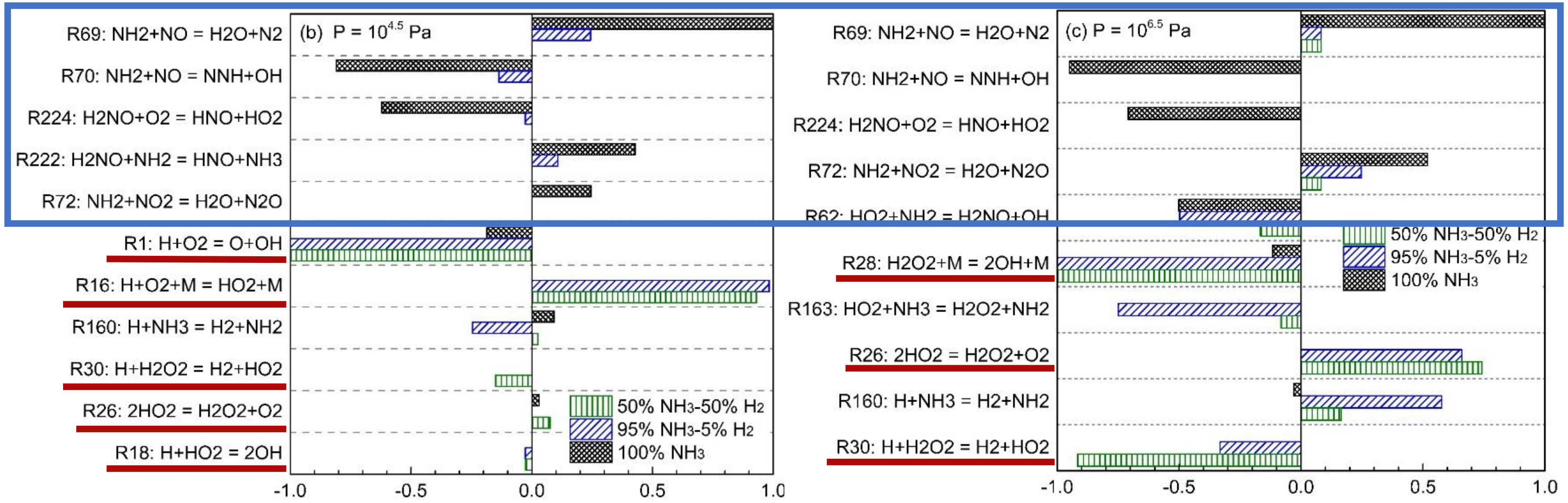
Lower explosion temperature at a given pressure

Sensitivity analysis: low pressure



- **Pure NH_3:** Reactions involving **hydronitrogen** are dominant. (e.g. R164, R160, R63, R118)
- **NH_3/H_2 mixtures:** **NH_2-related** reactions are dominant. (e.g. R160, R56, R70, R86, R57)

Sensitivity analysis: elevated pressures



- **Pure NH_3:** Reactions involving **NH_2, nitrous oxides and H_2NO** play an important role.
- **NH_3/H_2 mixtures:** **H_2-O_2 system reactions** have significant effects; Reactions involving **H_2O_2 and HO_2** are enhanced.

Eigenvalue analysis: mechanism construction

Molecule-molecule reactions

Mech 2
26 species
82 reactions

Radical-molecule reactions

Linear mechanism (Linear Mech)

No.	Reaction	No.	Reaction
R1	$H + O_2 = O + OH$	R10	$NH_2 + O_2 = HNO + OH$
R2	$H_2 + O = H + OH$	R11	$NH_3 + M = H + NH_2 + M$
R3	$H_2 + OH = H + H_2O$	R12	$H + NH_3 = H_2 + NH_2$
R4	$H + O_2 + M = HO_2 + M$	R13	$NH_3 + O = NH_2 + OH$
R5	$H + HO_2 = H_2 + O_2$	R14	$NH_3 + OH = H_2O + NH_2$
R6	$H_2O_2 + M = 2OH + M$	R15	$HO_2 + NH_3 = H_2O_2 + NH_2$
R7	$H + H_2O_2 = H_2 + HO_2$	R16	$HNO + O_2 = HO_2 + NO$
R8	$HO_2 + NH_2 = NH_3 + O_2$	R17	$HNO + NH_2 = NH_3 + NO$
R9	$NH_2 + O_2 = H_2NO + O$	R18	$H_2NO + O_2 = HNO + HO_2$

Eigenvalue analysis: matrix establishment

Wall destruction reactions

$$R \overset{k_R}{\rightarrow} absorbed\ products \qquad k_R = \frac{1}{4}\varepsilon\bar{v}\frac{S}{V}$$

Competition coefficients (between NH_3 and H_2)

For O
- R2: $\mathbf{H_2}$ + O = H + OH
- R13: $\mathbf{NH_3}$ + O = NH_2 + OH

$$\alpha = \frac{k_2[H_2]}{k_2[H_2]\ + k_{13}[NH_3]}$$

For OH
- R3: $\mathbf{H_2}$ + OH = H + H_2O
- R14: $\mathbf{NH_3}$ + OH = H_2O + NH_2

$$\beta = \frac{k_3[H_2]}{k_3[H_2]\ + k_{14}[NH_3]}$$

For HO_2
- R7: H + H_2O_2 = $\mathbf{H_2}$ + HO_2
- R15: HO_2 + $\mathbf{NH_3}$ = H_2O_2 + NH_2

$$\gamma = \frac{k_{7r}[H_2]}{k_{7r}[H_2]\ + k_{15}[NH_3]}$$

Eigenvalue analysis: matrix establishment

The system of ordinary differential equations

$$([H], [HO_2], [H_2O_2], [NH_2])^T$$

$$\frac{dX}{dt} = \boldsymbol{LX} + \boldsymbol{N}$$

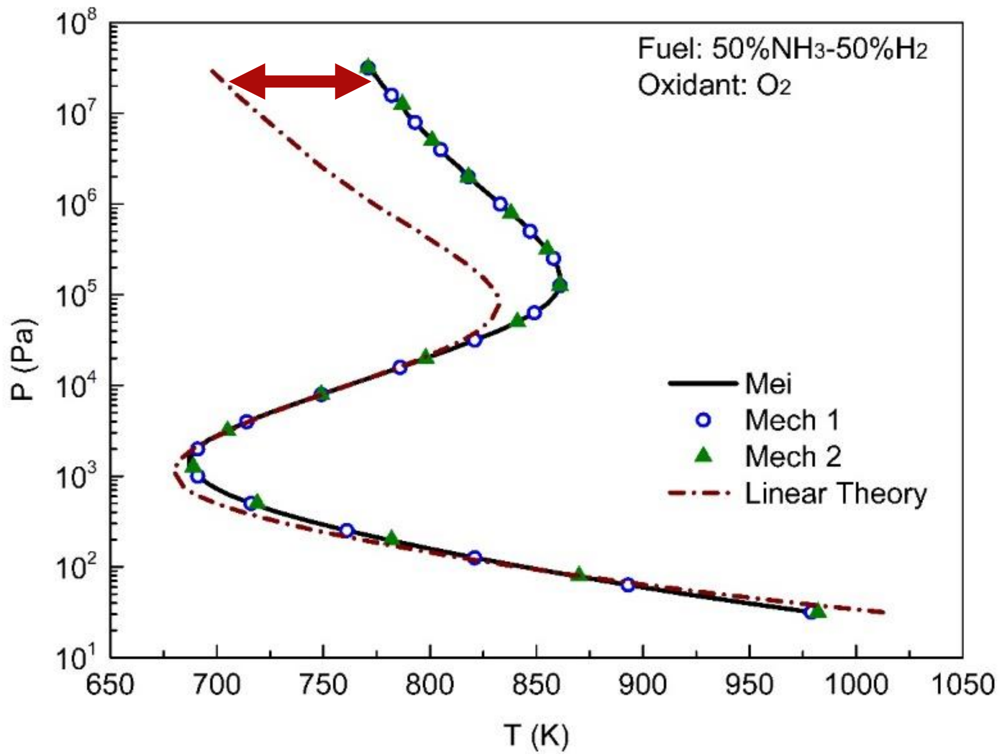
$$\boldsymbol{N} = \begin{bmatrix} k_{5r}[H_2][O_2] + k_{11}[NH_3][M] \\ k_{5r}[H_2][O_2] + k_{8r}[NH_3][O_2] \\ 0 \\ k_{8r}[NH_3][O_2] + k_{11}[NH_3][M] \end{bmatrix}$$

$$\boldsymbol{L} = \begin{bmatrix} (\alpha + 2\beta - 1)k_1[O_2] - k_4[O_2][M] - k_{12}[NH_3] - k_H & k_{7r}[H_2] & 2\beta k_6[M] & k_{12r}[H_2] + (\alpha + \beta)k_9[O_2] + \beta k_{10}[O_2] \\ k_4[O_2][M] & -\frac{k_{7r}[H_2]}{\gamma} - k_{HO_2} & 0 & 2k_9[O_2] + k_{10}[O_2] \\ 0 & \frac{k_{7r}[H_2]}{\gamma} & -k_6[M] - k_{H_2O_2} & 0 \\ (3 - \alpha - 2\beta)k_1[O_2] + k_{12}[NH_3] & k_{15}[NH_3] & 2(1 - \beta)k_6[M] & (1 - \alpha - \beta)k_9[O_2] - \beta k_{10}[O_2] - k_{12r}[H_2] - k_{NH_2} \end{bmatrix}$$

Eigenvalue analysis: linear theory

Explosion criterion: $det(L) = 0$

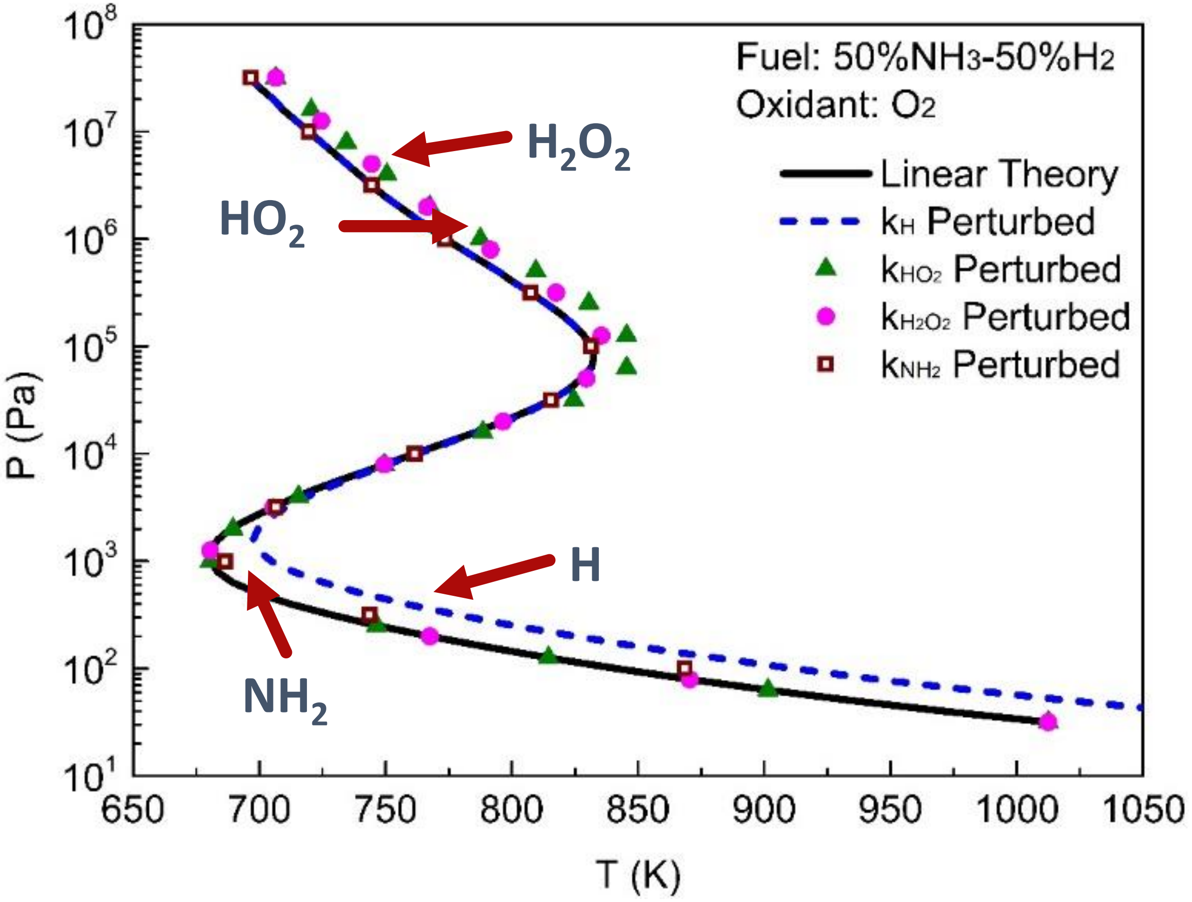
Ideal gas assumption: $[M] = P/R_0T$



Linear Theory:

- Agrees well at the first and second limits
- Deviates at the third limit

Wall destruction effects



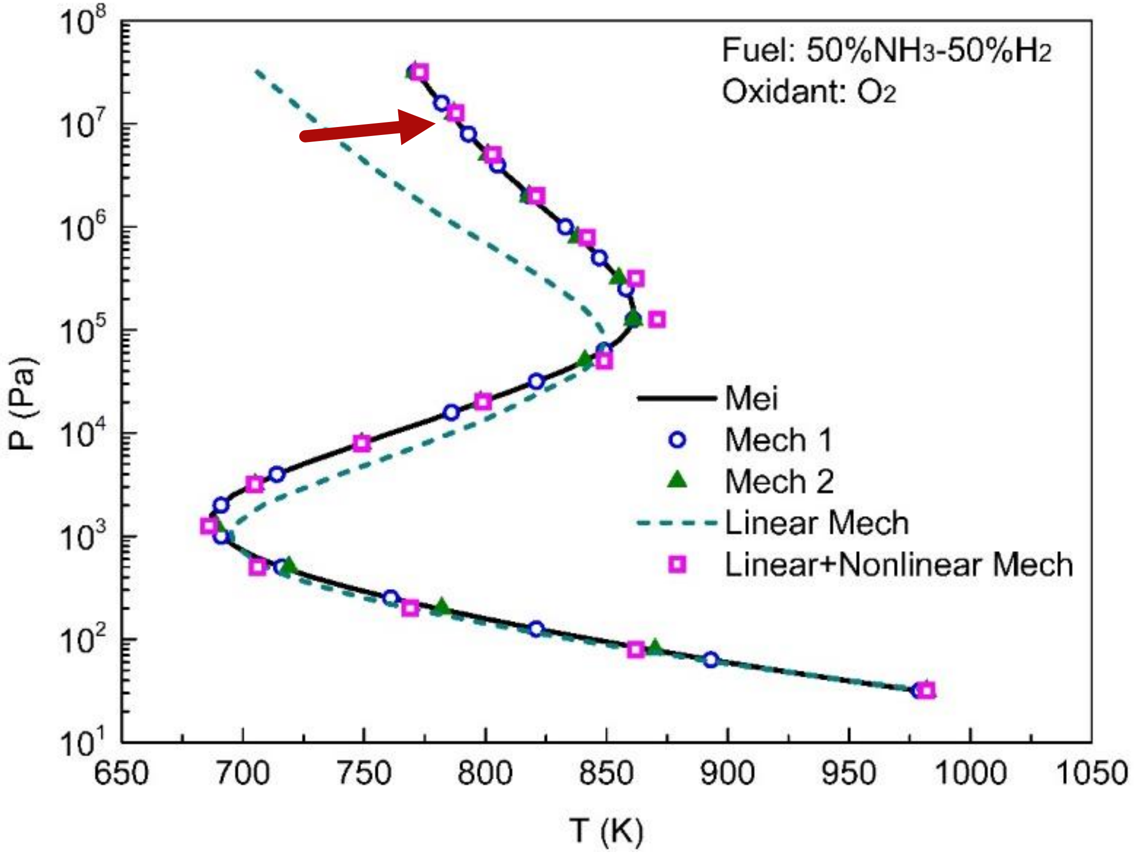
- H and NH$_2$ destruction influences the first limit.
- HO$_2$ and H$_2$O$_2$ destruction influences the third limit.

Modified mechanism

Non-linear mechanism: reactions between intermediate species

Non-linear Mech

No.	Reaction
R19	$H + HO_2 = 2OH$
R20	$2HO_2 = H_2O_2 + O_2$
R21	$H + H_2O_2 = H_2O + OH$
R22	$HO_2 + NH_2 = H_2NO + OH$



Summary Part I

- The monotonic explosion limit curve of pure NH_3 turns into a nonmonotonic one with H_2 addition.
- For pure NH_3, the reactions involving hydronitrogen are dominant at low pressures, and the reactions involving NO, NO_2, HNO and H_2NO become more significant with elevated pressure.
- As H_2 percentage increases, H_2-O_2 system reactions become dominant at medium and high pressures, and the reactions involving H_2O_2 and HO_2 play a significant role at high pressures.
- Wall destruction of HO_2 and H_2O_2 obviously influences the third limit, while that of H and NH_2 affects the first limit.
- A compact mechanism is constructed to calculate the explosion limits of NH_3/H_2 mixtures.

Part II: Energy Conversion in Premixed Flames of Hydrogen/Ammonia Mixtures

Combustion efficiency: Energy Conversion

Energy Analysis

First-law Thermodynamics → Quantity

Second-law Thermodynamics → Quality

This talk

1st Law Energy Balance

Work	Heat Loss	Exhaust Energy
Total Fuel Energy		

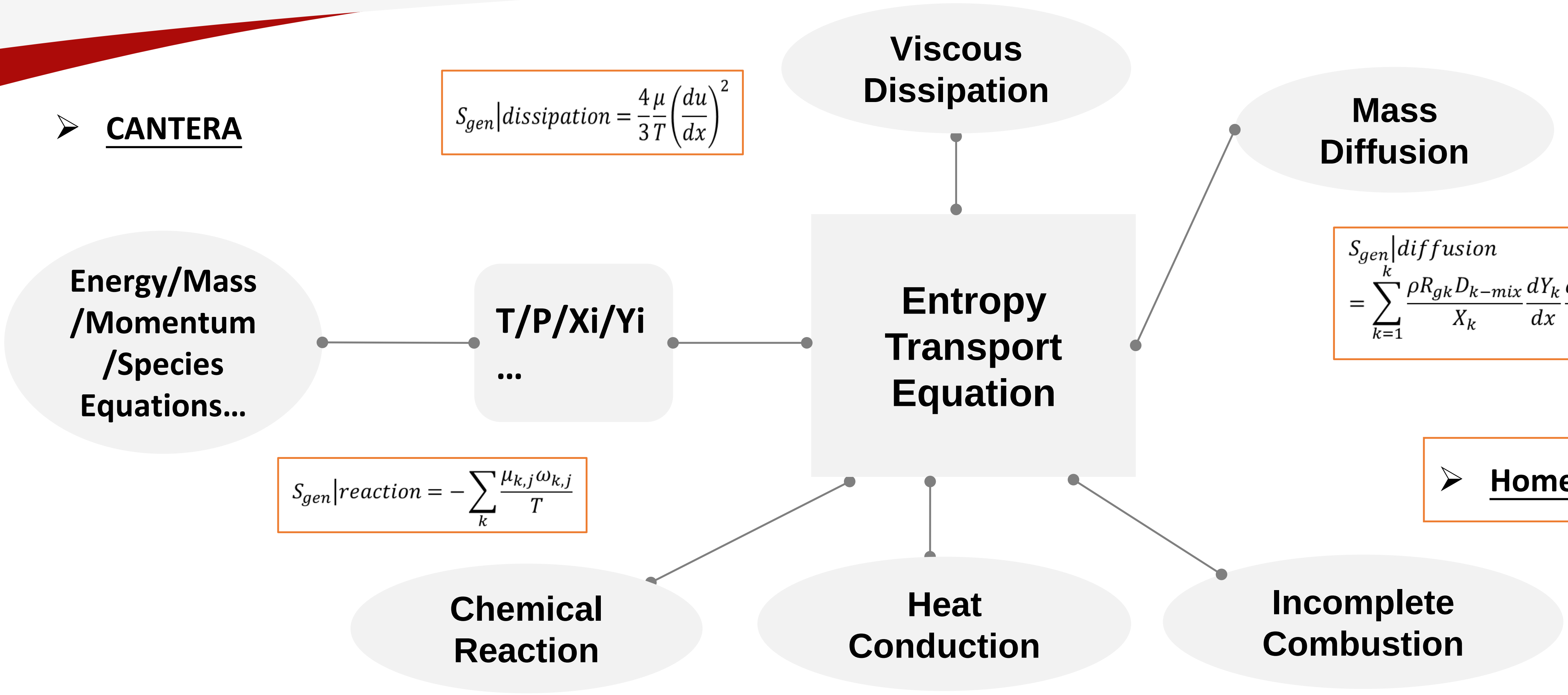
2nd Law Energy Balance

Work	Exergy Transfer due to Heat Loss	Exergy Loss	Exhaust Exergy
Total Fuel Exergy			

Methodology for the Exergy Loss Analysis

- **CANTERA**

$$S_{gen}\big|dissipation = \frac{4}{3}\frac{\mu}{T}\left(\frac{du}{dx}\right)^2$$



$$S_{gen}\big|diffusion = \sum_{k=1}^{k} \frac{\rho R_{gk} D_{k-mix}}{X_k}\frac{dY_k}{dx}\frac{dX_k}{dx}$$

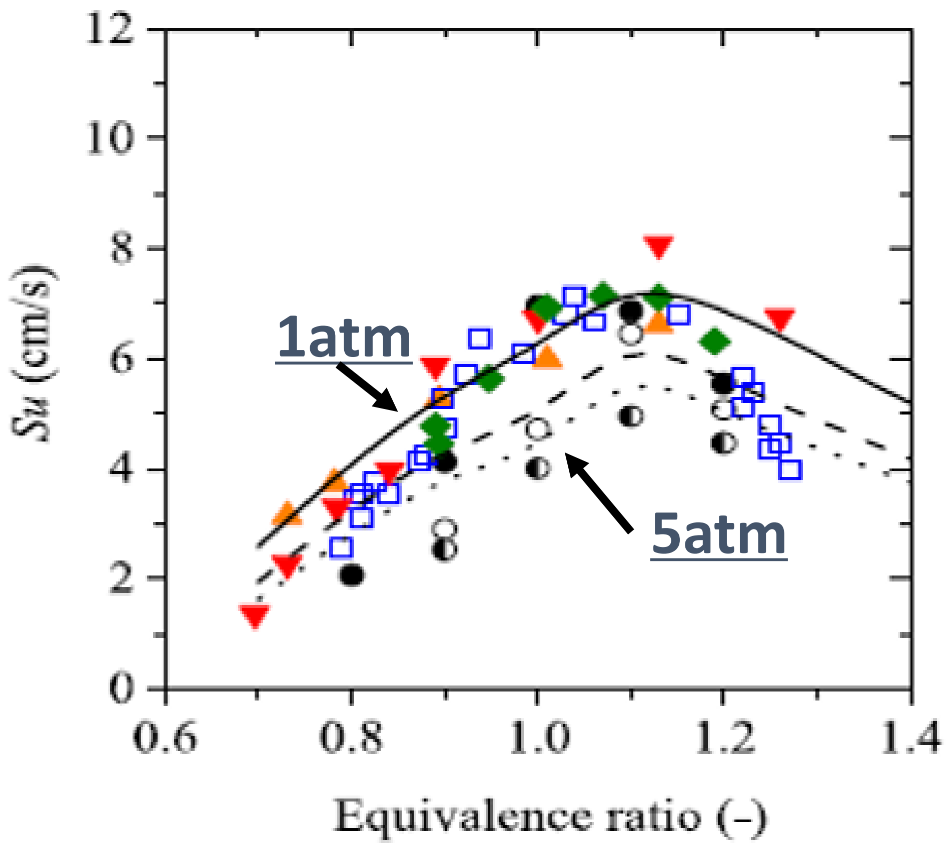
$$S_{gen}\big|reaction = -\sum_{k}\frac{\mu_{k,j}\omega_{k,j}}{T}$$

- **Homemade code**

$$S_{gen}\big|conduction = \lambda\frac{1}{T^2}\left(\frac{dT}{dx}\right)^2$$

$$E_{inloss} = \sum_{com,pro} G - \sum_{incom,pro} G$$

Calculation Specification



Initial Temperature: 298K

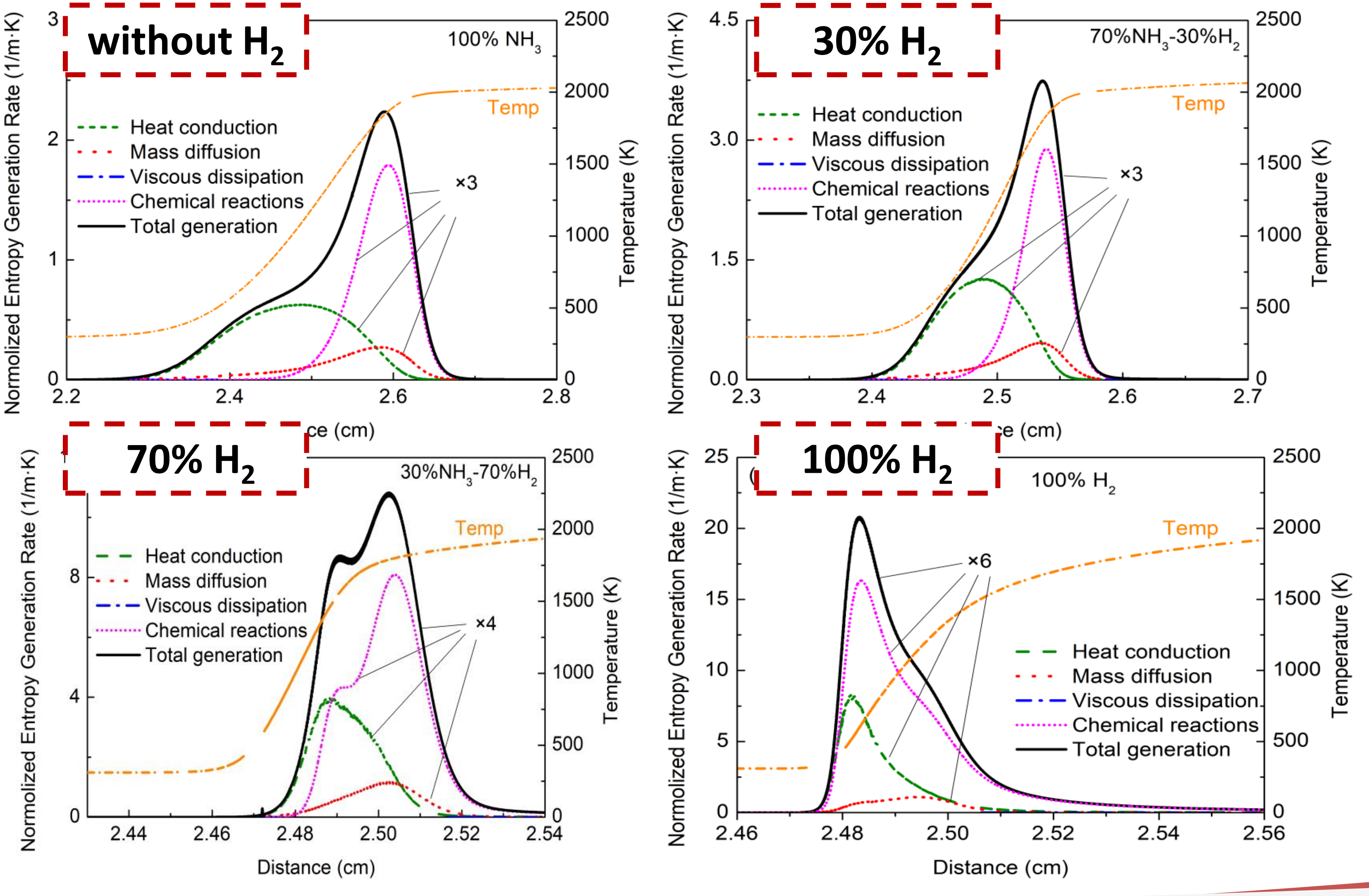
Equivalence ratio: 1.0

Initial Pressure: 1atm, 5atm

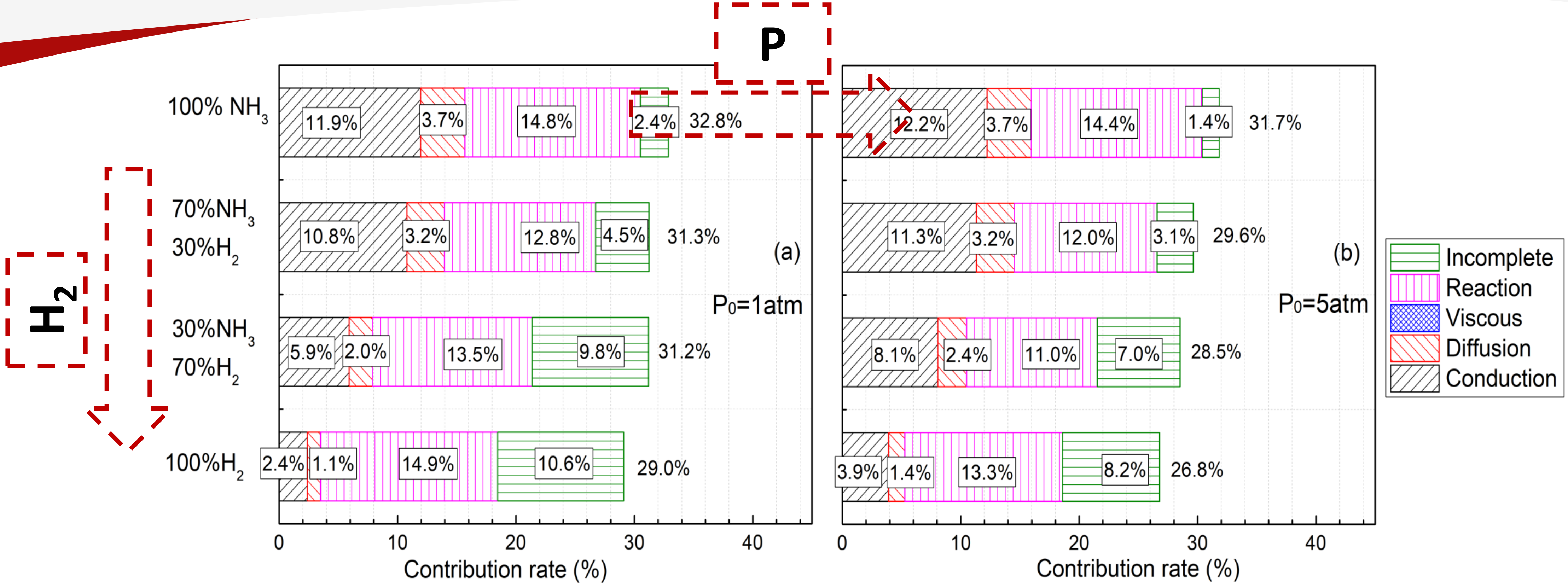
Blending ratios: 100% NH_3, 70% NH_3 / 30% H_2, 30% NH_3 / 70% H_2, 100% H_2

Mechanism: Ammonia/Hydrogen Mixtures，Otomo et al. 36 species, 213 reactions.

Overview of the Exergy Loss

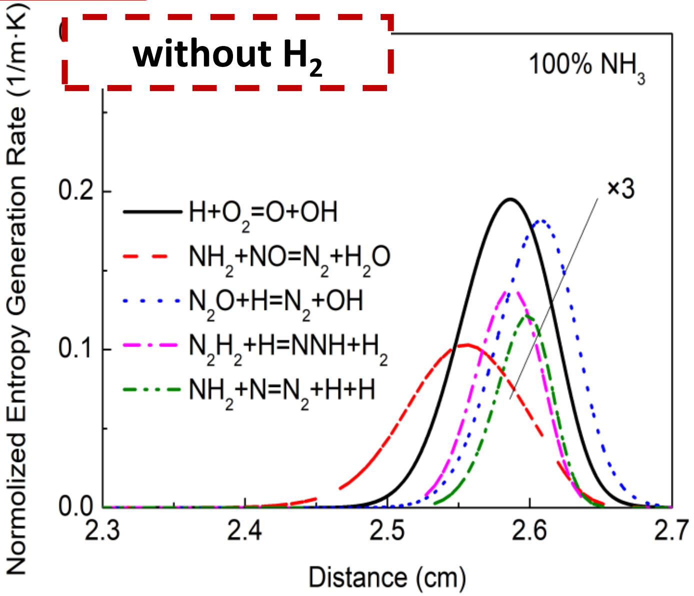


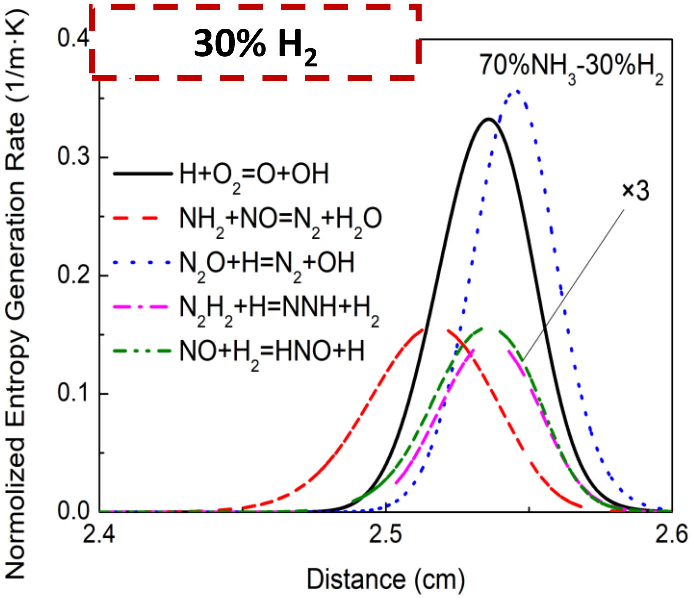
Overview of the Exergy Loss

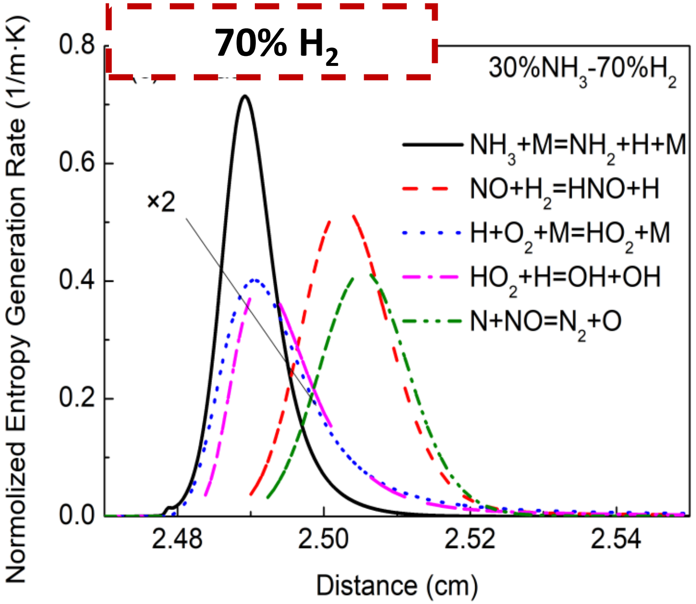


- The exergy loss due to chemical reaction decreases firstly and then increases.
- The exergy losses by mass diffusion and heat conduction decreases.
- The exergy loss decreases with increased H_2 percentage and increased initial pressure.

Chemical Reactions







N-dominated Reactions

100% NH_3 70% NH_3-30% H_2

Reactions generating N_2 contribute most to the exergy loss.

$H + O_2 = O + OH$

$NH_2 + NO = N_2 + H_2O$

$N_2O + H = N_2 + OH$

$N_2H_2 + H = NNH + H_2$

$NH_2 + N = N_2 + H + H$

$NO + H_2 = HNO + H$

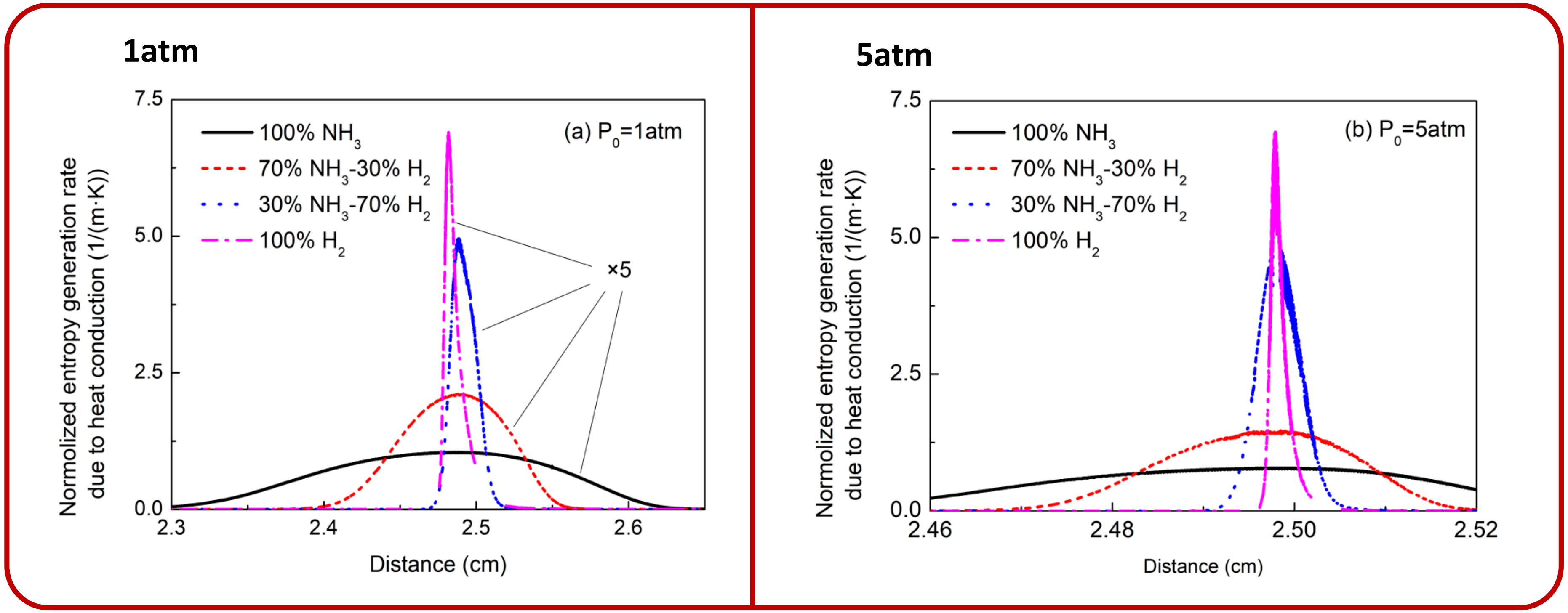
H_2-dominated Reactions

100% H_2 30% NH_3-70% H_2

$H + O_2 + M = HO_2 + M$

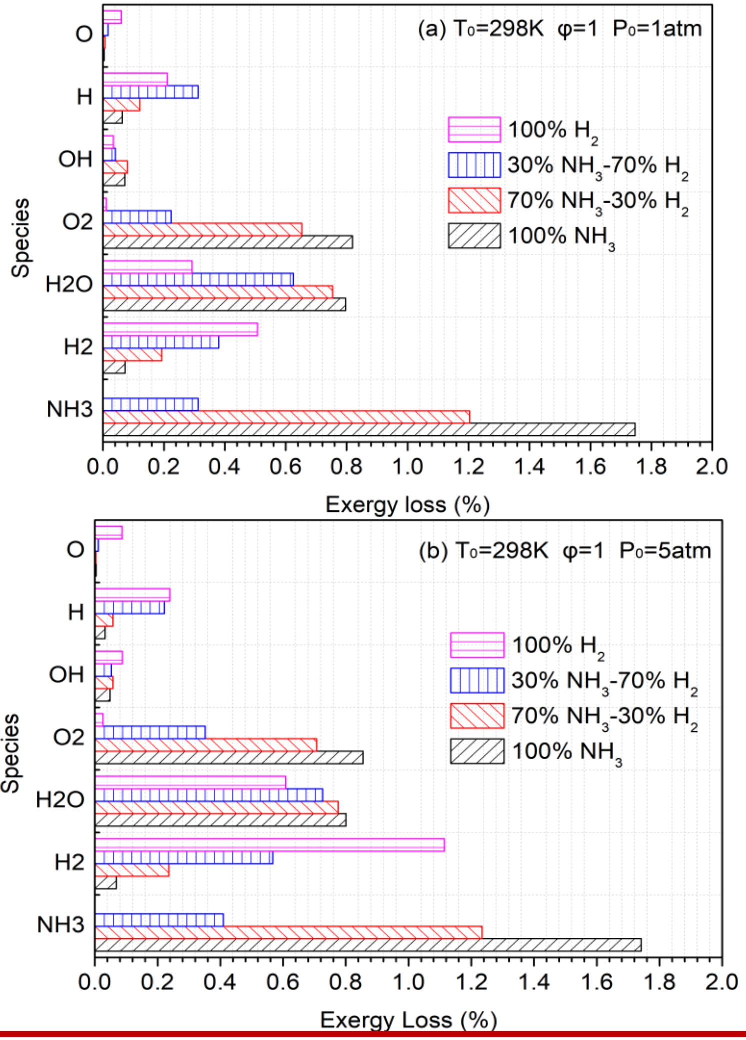
$HO_2 + H = OH + OH$

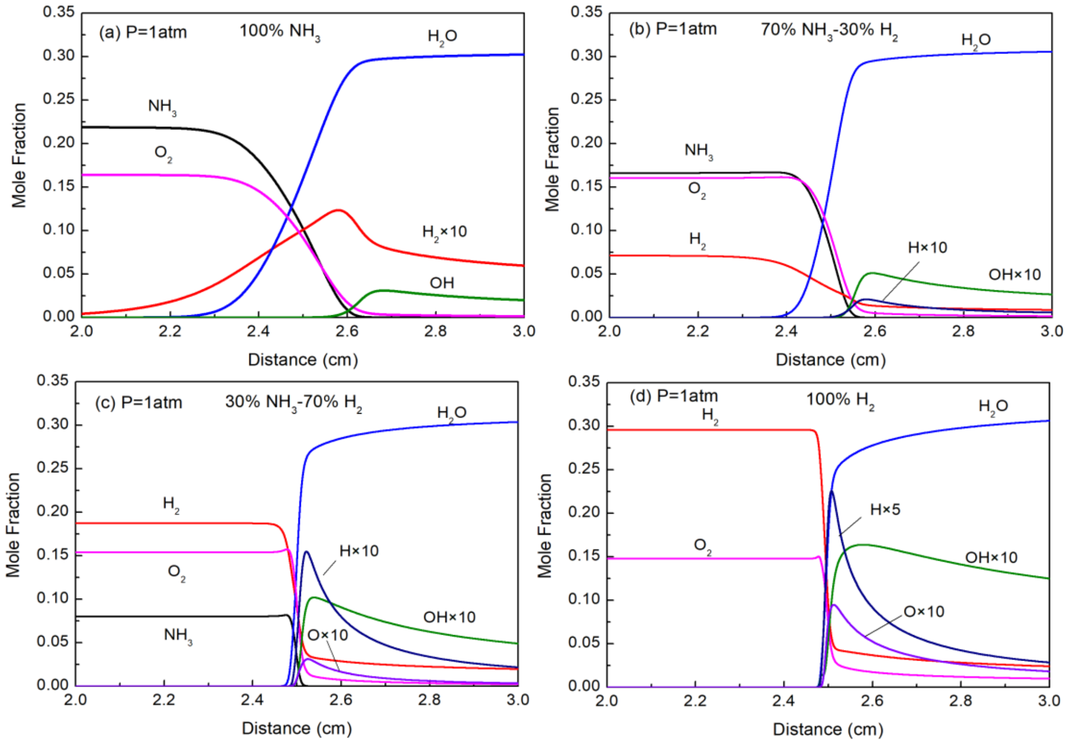
Heat Conduction



- The decrease of the flame thickness is more obvious than the increase of the exergy loss rate, thus leading to the decrease of the exergy loss due to heat conduction.
- Similar trends are observed at high pressure condition.

Mass Diffusion





Most contributed species: Reactants (NH_3, H_2, O_2), Products (H_2O), Active radicals (H, OH, O)

Incomplete Combustion

Pressure	Fuel composition	NH_3	H_2	H	O	OH
1 atm	100% NH_3	7.5×10^{-7}	4.9×10^{-3}	1.8×10^{-4}	3.1×10^{-5}	1.4×10^{-3}
	70% NH_3/30% H_2	1.6×10^{-8}	7.4×10^{-3}	3.2×10^{-4}	5.2×10^{-5}	1.9×10^{-3}
	30% NH_3/70% H_2	5.9×10^{-8}	1.6×10^{-2}	9.0×10^{-4}	1.0×10^{-4}	2.8×10^{-3}
	100% H_2	0	1.7×10^{-2}	2.0×10^{-3}	6.8×10^{-4}	8.5×10^{-3}
5 atm	100% NH_3	1.3×10^{-8}	3.0×10^{-3}	6.8×10^{-5}	1.3×10^{-5}	8.9×10^{-4}
	70% NH_3/30% H_2	2.4×10^{-8}	4.4×10^{-3}	7.0×10^{-4}	2.4×10^{-5}	1.3×10^{-3}
	30% NH_3/70% H_2	9.9×10^{-8}	9.7×10^{-3}	6.5×10^{-4}	4.7×10^{-5}	2.0×10^{-3}
	100% H_2	0	1.0×10^{-2}	8.4×10^{-4}	2.9×10^{-4}	5.8×10^{-3}

H_2

Summary Part II

- The total exergy loss of ammonia premixed flames decreases monotonically as hydrogen percentage in fuel blends.
- The overall exergy loss decreases by 1 - 2% as the pressure increased from 1atm to 5atm.
- The exergy destruction by chemical reactions first decreases and then increases with the increasing hydrogen percentage.
- The exergy destructions induced by heat conduction and mass diffusion decreases with the increasing hydrogen percentage.
- The exergy loss induced by incomplete combustion increases with hydrogen addition.

Thanks for your attention！