Chemical kinetics study of combustion characteristics of ammonia-air mixtures under high pressure lean conditions

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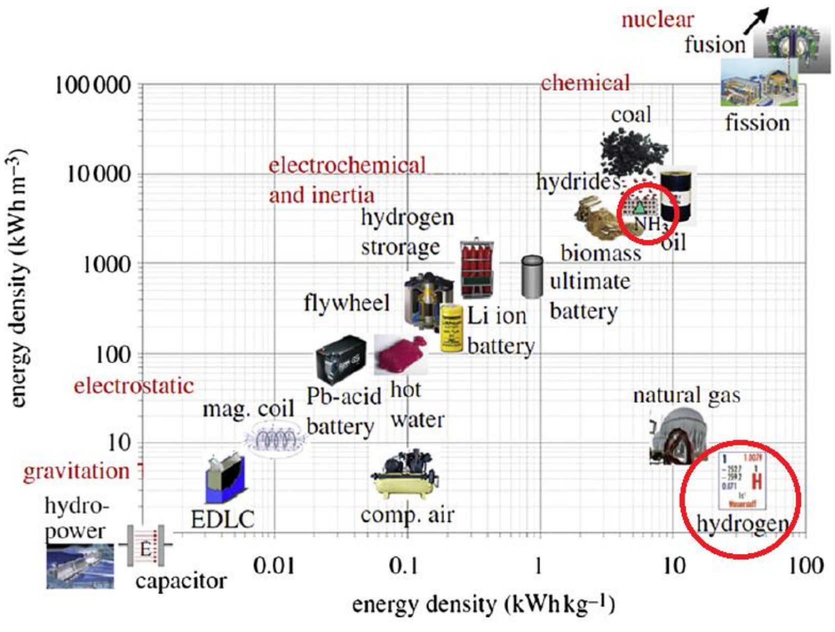
WHY NH_3

- **Low-cost storage (like propane storage conditions)**

- **Higher volumetric energy density**



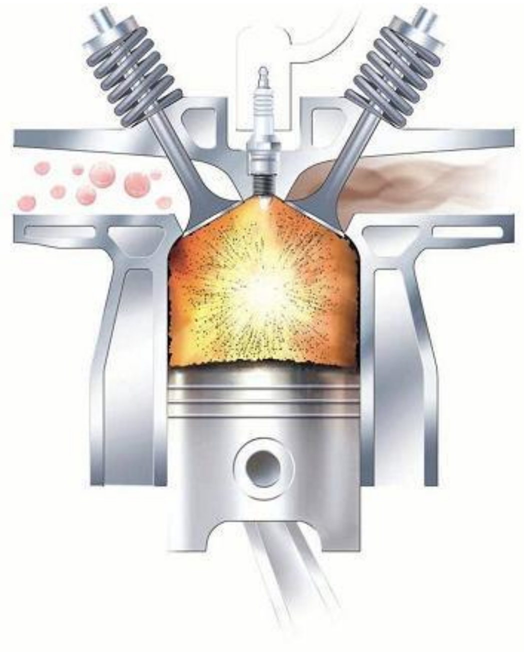
Ref: «Ammonia and related chemicals as potential indirect hydrogen storage materials», By R. Lan et al., 2012

WHY NH_3

Power generation capacity

Fuel	Fuel/air ratio*	Tcombuster* K at 20atm	Texhaust K at 1 atm	Enthalpy change (work) kJ/kg
Methane	0.058	2277	1260	1551
JP-4	0.068	2342	1313	1539
Ethanol	0.111	2295	1289	1546
NH3	0.164	2092	1114	1549

* Stoichiometric fuel/air combustion at a pressure ratio of 20:1

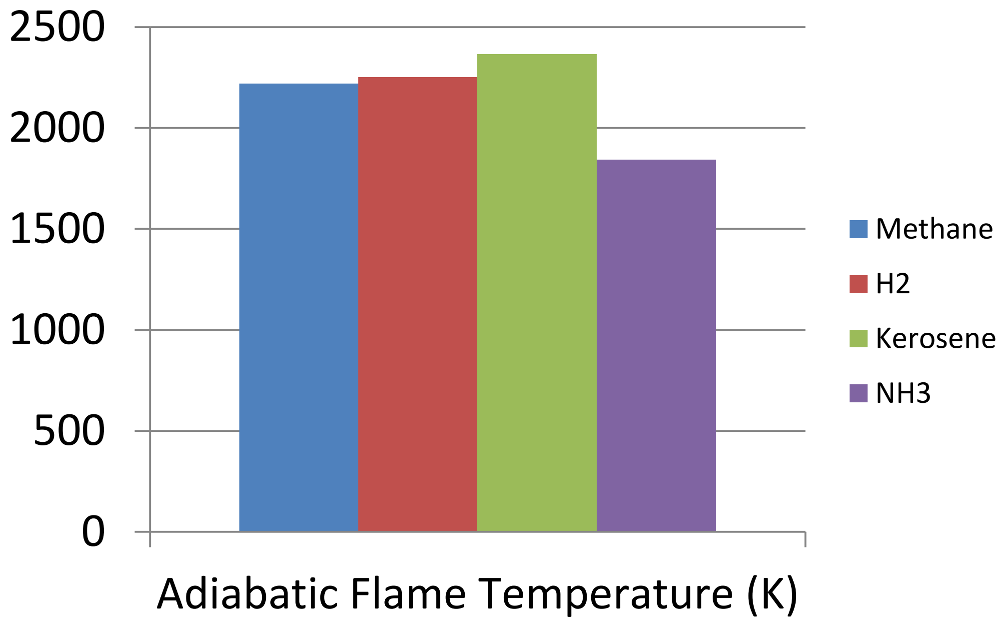


Ref: «Fuel Conditioning System for Ammonia-Fired Power Plants » By Arif Karabeyoğlu , Brian Evans, 2012

Drawbacks also exist!

MAIN CHALLENGES

- Low flame temperature and slow kinetics



1 atm and 20°C

«Ammonia – It's Transformation and Effective Utilization» AIAA 2008

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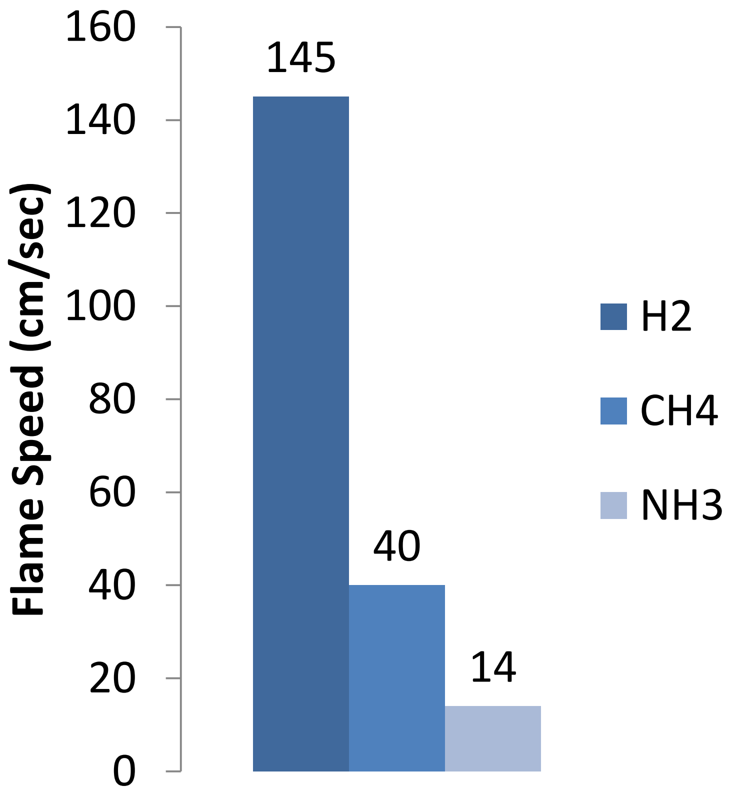
MAIN CHALLENGES

- Low flame speed



Standard Temperature and Pressure
Air as oxidizer

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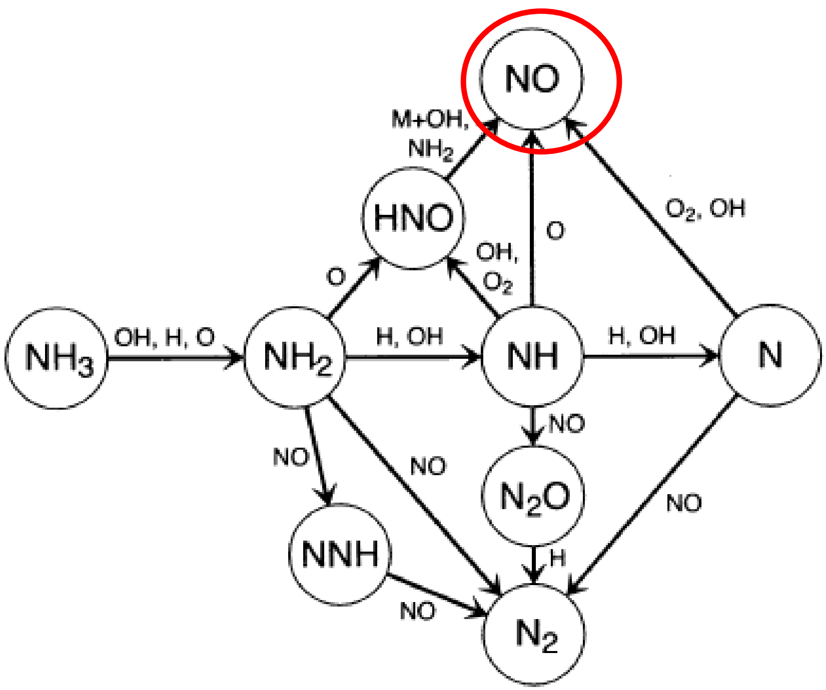
MAIN CHALLENGES

- NH_3 , A SOURCE OF NOx IN FLAMES

- Fuel NOx



A simplified reaction mechanism

Ref: Miller, J. A. et al. , Combust. Sci. Tech., 34:149–176 (1983)

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OBJECTIVES AND APPROACH

Objective

- To burn NH_3 in a power generation system in efficient and environmentally friendly way:
  - Low NO_x emission
  - Low NH_3 slip

Approach

- Chemical kinetics study of NH_3/H_2/Air under practical combustion conditions
- Developing a reduced mechanism capable of predicting combustion characteristics with an acceptable accuracy
- CFD simulation of combustion by applying the reduced mechanism
- Experimental study to examine the validity of results

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NUMERICAL STUDY CONDITIONS

NH3/H2/Air

$$xNH_3 + yH_2 + a_{stoi}(O_2 + 3.76\,N_2) \rightarrow b\,H_2O + c\,N_2$$

P=17 atm

ϕ=0.5

(gas turbine condition)

Studied Cases	Reactants' Composition			
% E of NH_3	NH_3	H_2	O_2	N_2
100	0.1228	0	0.1843	0.6929
80	0.0958	0.0382	0.1819	0.6840
60	0.0701	0.0745	0.1797	0.6757
40	0.0456	0.1091	0.1776	0.6677
20	0.0223	0.1421	0.1755	0.6600
0	0	0.1736	0.1736	0.6528

$$\%E\ NH3 = \frac{X_{NH3} \times LHV_{NH3}}{X_{NH3} \times LHV_{NH3} + X_{H2} \times LHV_{H2}} \times 100$$

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STUDY SCOPE

- Laminar flame speed sensitivity analysis
- Autoignition process
- NOx formation sensitivity analysis
- Impact of variation of main parameters on total NOx level

REACTION MECHANISM

Konnov Mechanism*
Elements: N/H/O
Species: 30
Reactions: 240

* A.A.Konnov, Combust. Flame 156 (2009) 2093–2105

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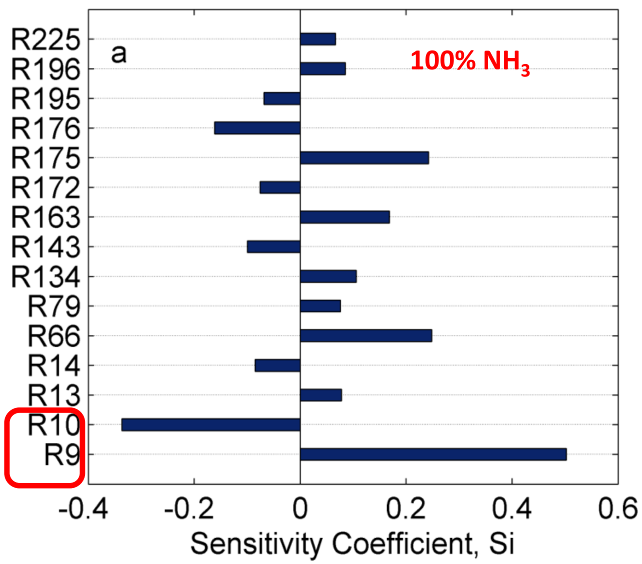
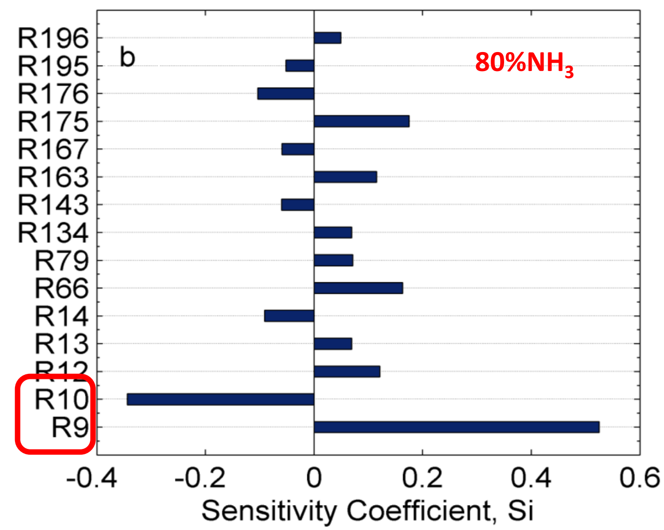
RESULTS

Laminar flame speed sensitivity analysis

Aim: To identify the most influential reactions to the laminar flame speed



R9: $H+O_2 \leftrightarrow OH+O$
R10: $H+O_2 \leftrightarrow HO_2$



$$S_i = (A_i/S_u) \times (\partial S_u/\partial A_i)$$

S_i: Normalized sensitivity coefficient of the i[th] reaction
A_i: Pre-exponential rate constant of the i[th] reaction
S_u: Laminar flame speed

ϕ = 0.5, P=17 bar, T= 673 K

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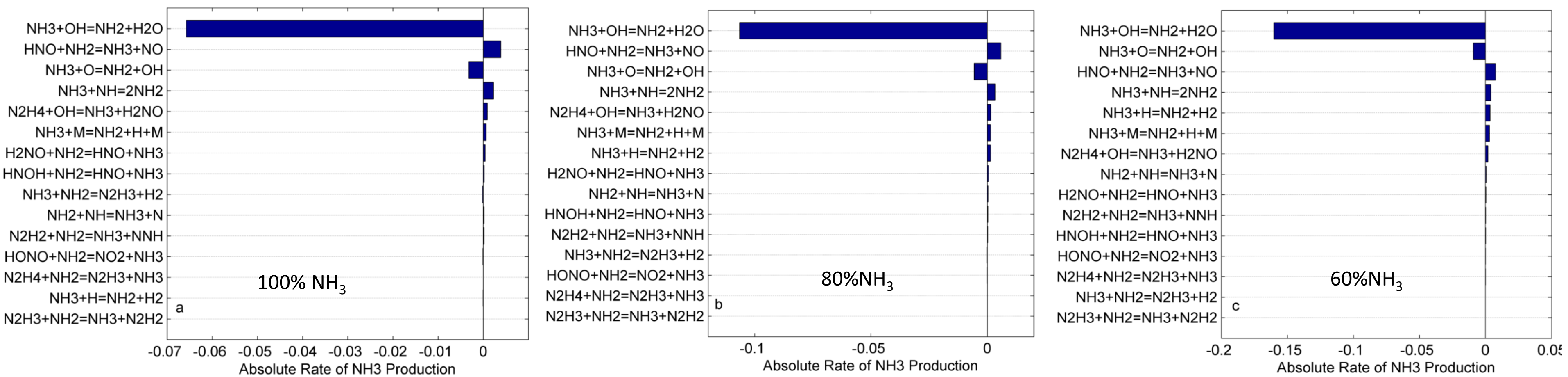
RESULTS

Ammonia decomposition analysis

Aim: To identify the contribution of each reaction in molar conversion of NH_3



Study Cases	The most important reactions and their contribution (%)		
Fuel mixture	$NH_3+OH \leftrightarrow NH_2+H_2O$	$NH_3+O \leftrightarrow NH_2+OH$	$NH_3+NH_2 \leftrightarrow N_2H_3+H_2$
Pure NH_3	95%	4.64%	0.23%
80%NH_3	94.8%	5.04%	0.11%
60%NH_3	94.5%	5.45%	ignorable

ϕ = 0.5, P=17 bar, T= 673 K

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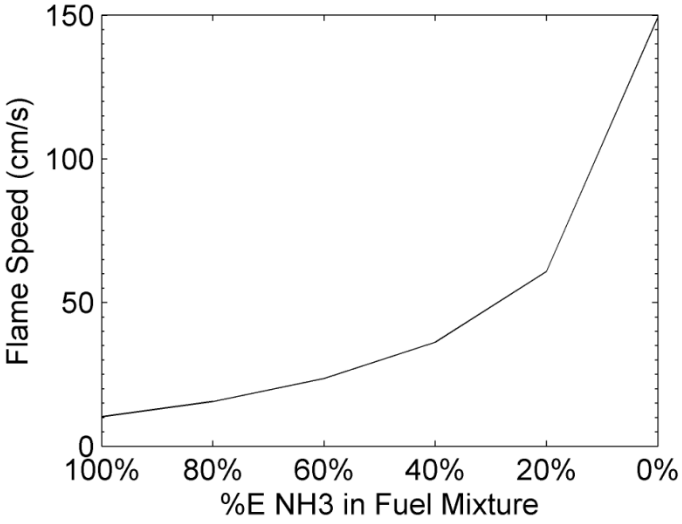
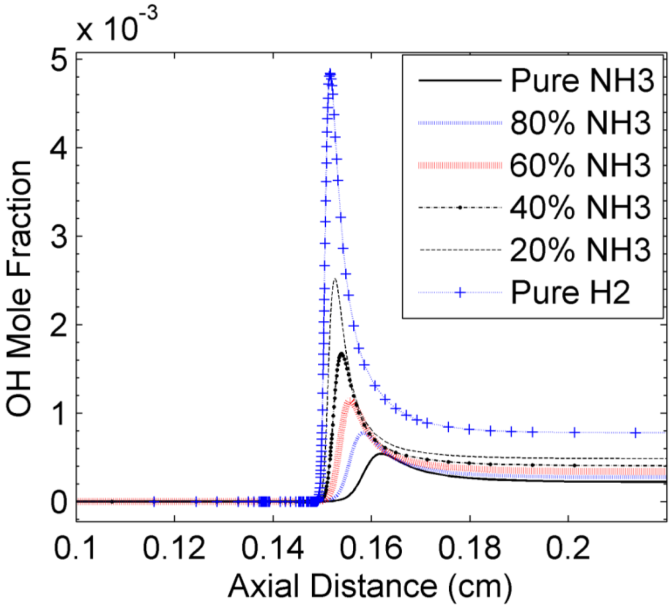
RESULTS

Importance of OH radical in flame speed



Correlation



ϕ = 0.5, P=17 bar, T= 673 K

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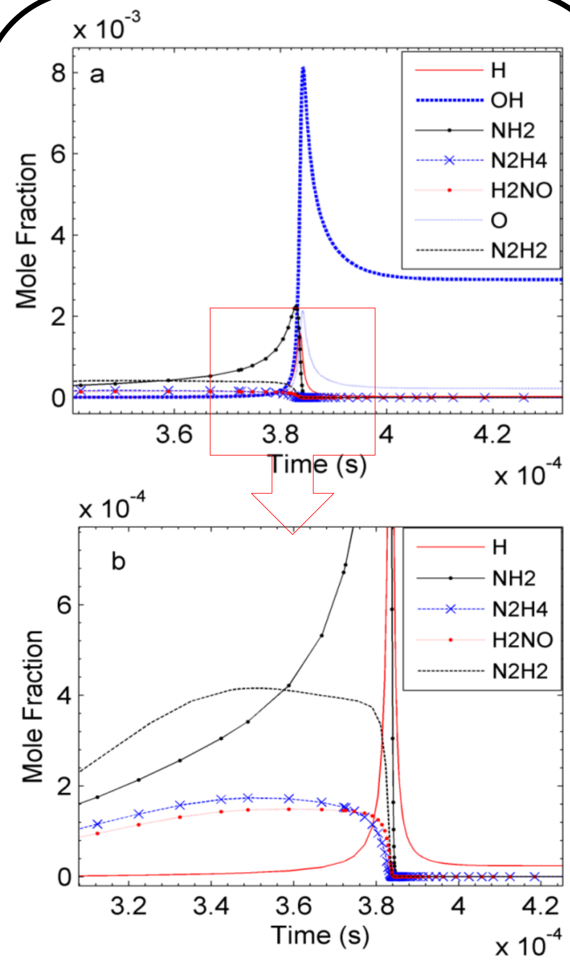
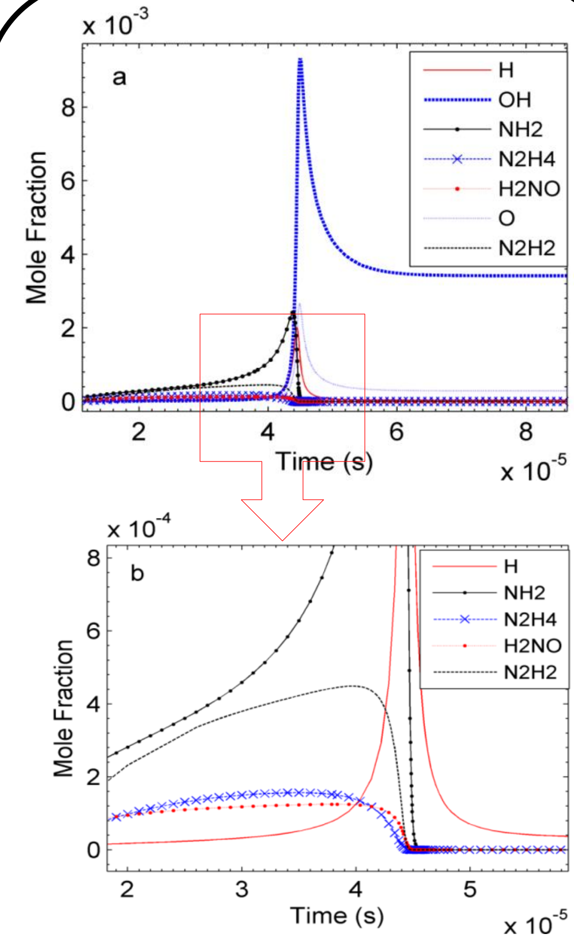
RESULTS

Autoignition

Importance of radicals in autoignition and ignition initiation



100%NH_3



80%NH_3

Accumulation of influential radicals close to the ignition time

ϕ=0.5, T=1300 K, P=17 bar

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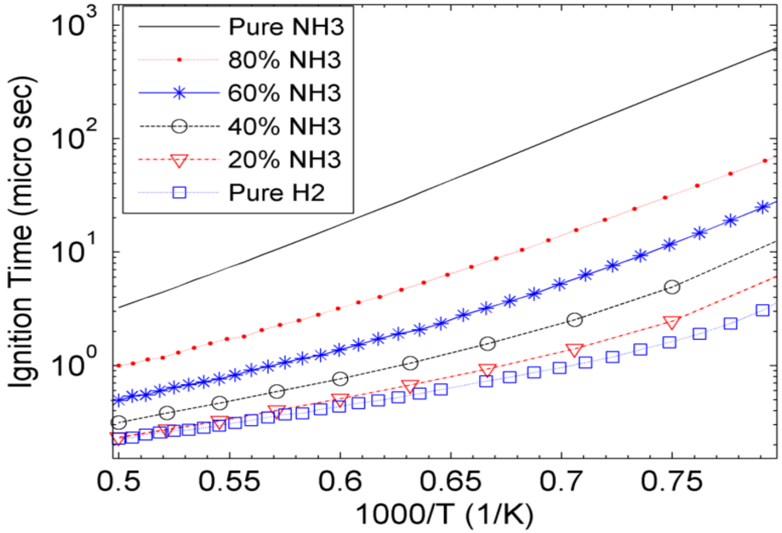
RESULTS

Autoignition

- Effect of initial mixture T
- Effect of NH3 content



ϕ=0.5, P=17 bar

RESULTS

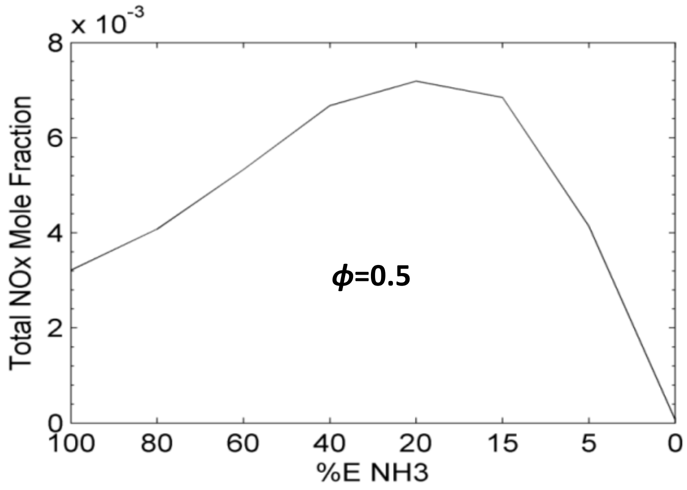
NOx Formation

Effect of H2 addition to the mixture

- Addition up to 80%
  - Increase in total NOx

    Thermal NOx increase>Fuel NOx decrease
- Higher than 80% H2
  - Decrease in total NOx

    Fuel NOx decrease>Thermal NOx increase



RESULTS

NOx Formation

Effect of equivalence ratio variation

- Increasing / Decreasing trend

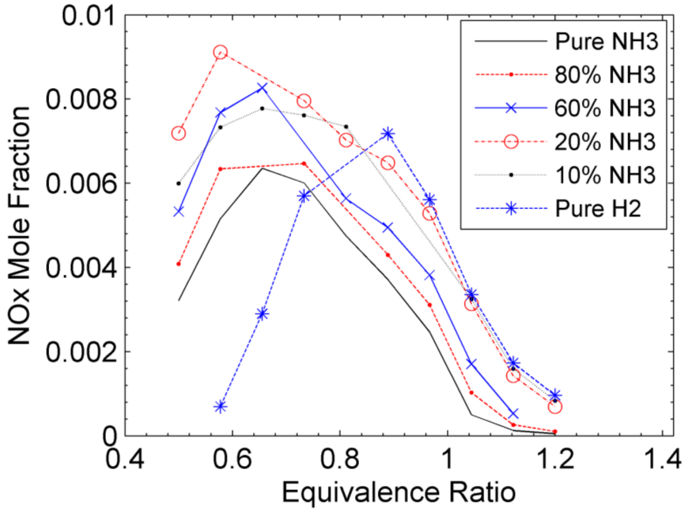
Two opposite effects:

1) Increase in thermal NOx by increase in adiabatic flame T

2) Decreasing fuel NOx by decreasing O/F ratio

$$NH_i + OX \rightarrow NO + H_iX$$

OX: Oxygenated species



Noticeable reduction in NO_x emission under the rich conditions

P=17 bar, T=673 K

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CONCLUDING REMARKS

Under the studied conditions

- Controlling role of radicals in laminar flame speed and autoignition process with OH as the most influential radical
- Adding H2 to the fuel mixture improved laminar flame speed and autoignition process
- Adding H2 does not necessarily decrease the NOx level
- Total NOx formation is highly dependent on the **competition** between **fuel NO_x** and **thermal NO_x** levels
- NOx level is very sensitive to equivalence ratio in all the mixture compositions
- **Localized rich combustion** seems to minimize NOx. Ammonia slip may be the compromise

FUTURE RESEARCH

- Obtaining a reduced mechanism applicable to CFD codes
- CFD simulation of the combustion process using the resulted reduced mechanism
- Experimental investigation of NH3 combustion in combustor of a power generation unit

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Thank You

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